

the XIXth edition of the  
**INTERNATIONAL CONFERENCE**  
**"STUDENTS FOR STUDENTS"**



**BOOK OF ABSTRACTS**  
**2023**





**19<sup>th</sup> edition of the  
INTERNATIONAL CONFERENCE  
“STUDENTS FOR STUDENTS”**

**Book of Abstracts**

**26<sup>th</sup> – 30<sup>th</sup> of April 2023**

## *Preface*

On behalf of Chemistry Students' Organization, in partnership with Faculty of Chemistry and Chemical Engineering from Babeş-Bolyai University Cluj-Napoca, it is our pleasure to welcome you to the XIX<sup>th</sup> edition of the INTERNATIONAL CONFERENCE "STUDENTS FOR STUDENTS" which will take place between the 26<sup>th</sup> and the 30<sup>th</sup> of April 2023.

The International Conference "*Students for Students*" is a program developed by our organization that has the aim of gathering together students from all around the world offering them the chance to present their work, develop their communication skills and exchange ideas with other young researchers. We want to encourage and promote scientific research among young students and create a conducive environment where the world can benefit from their research. The program also offers a series of lectures and presentations held by important speakers from inside and outside the country, with the purpose of familiarizing the participants with the latest info on their fields of interest.

The conference is divided into 2 categories (Undergraduate and Master) and 2 sections for each category (Poster/Flash Presentation, and Presentations on Chemistry, Chemical Engineering, or other sciences with applications in Chemistry and/or Chemical Engineering). The participants can choose to present their work as a poster or as an oral presentation for any of the above-mentioned sections.

This year, there are 48 students, from all around the world, that registered in our conference, with 19 posters, and 27 oral presentations, in which 6 are for chemical engineering, 35 are for chemistry and 5 are for other sciences with applications in chemistry and/or chemical engineering. We also have 3 distinguished speakers, invited to present their work in the fields of chemistry and chemical engineering, that we are very thankful for accepting our invitation. We also want to thank our professors and all the persons from Faculty of Chemistry and Chemical Engineering Cluj-Napoca, for helping the organizing committee bring this project together. We are extremely grateful for all the support and very excited to experience this year's edition together.

## The Organizing Committee

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  - **Adriana-Flavia LUPEA** – Co-Coordinator and Censor of the Chemistry Students' Organization
  - **Amalia-Ioana PRODAN** – Co-Coordinator and active member of the Financiar department of the Chemistry Students' Organization
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  - **Dr. Dan PORUMB** member of the Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University

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# *INVITED COMMUNICATIONS*



## Transient species in biological metal centers and where to find them

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Compared to classical synthetic chemistry, biological reaction mechanisms generally face limitations imposed by the aqueous and (often) aerobic environments inside living cells. For instance, while in synthetic chemistry iron the oxidation states are known to span values from -4 to +7, the redox potentials inside living organisms would normally only allow for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  - and similar situations are seen with other transition metals. Likewise, the ligands for biological metal centers are inherently simple water-soluble organic compounds typically found inside living cells - amino acids, nucleotides, sugars, metabolites. However, biological metal centers also engage in a range of more exotic reactions, some of which even occur in/with living organisms. For instance,  $\text{Fe}^{4+}$ ,  $\text{Fe}^+$ ,  $\text{Co}^+$  and  $\text{Ni}^+$  are now well accepted to be involved in catalysis by enzymes. Exotic ligands such as hydrocarbons, hydrogen, or very unstable species such as halide/chalcogenide/nitrogen oxyanions (e.g., hypochlorite, chlorite, sulfur oxides), peroxides and others have been shown to form metastable adducts with biological metal centers, not only as an *in vitro* curiosity but also with physiological implications.

The search for exotic oxidation states and/or coordination states in biological metal centers typically entails techniques particularly adept at examining very unstable/transient species. Presented in this lecture will be examples from the author's work, where such techniques as stopped-flow UV-vis spectroscopy, freeze-quench coupled with low-temperature electron paramagnetic resonance - EPR - or Mössbauer spectroscopy, and computational chemistry (e.g., density functional calculations, DFT) were employed in order to detect and characterize unusual oxidation or coordination states in biological metal centers - in some cases with practical physiological/biomedical relevance.

## **Advanced energy conversion systems integrated with Carbon Capture, Utilization and Storage (CCUS) technologies**

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Energy and environmental issues are currently crucially important considering the double significance: (i) security of energy supply combined with decoupling the energy consumption from carbon emissions and (ii) global warming mitigation by reducing the greenhouse gas (GHG) emissions to achieve the climate neutrality. The rationale behind reducing GHG emissions is to keep average global temperature increase below 2°C compared with pre-industrial levels. Furthermore, EU climate and energy package [1] sets the following community targets by 2030: (i) Cutting greenhouse gases by at least 55% of 1990 levels; (ii) Cutting energy consumptions by 32.5% by improving energy efficiency; (iii) Increasing use of renewable to 32% of total production. Even further, according to European Green Deal [2] the European Union should be by 2050 a climate neutral region (no net GHG emissions).

To meet the challenges of energy security and climate change as well as the growing energy needs of the developing world, a global energy technology revolution is essential. A portfolio of key energy-efficient decarbonization technologies is to be developed to attain the emission targets. Among these technologies, Carbon Capture, Utilization and Storage (CCUS) has a special place. Broadly, there are three different conceptual ways for CO<sub>2</sub> scrubbing [3]:

- Post-combustion, in which the CO<sub>2</sub> is removed after combustion of the fossil / renewable fuel (from flue gases) using chemical gas-liquid absorption;

- Pre-combustion, in which the fossil / renewable fuel is partially oxidized, via gasification / reforming processes. The syngas is shifted into CO<sub>2</sub> and more H<sub>2</sub>, the resulting CO<sub>2</sub> is then captured. The H<sub>2</sub> can now be used as fuel;

- Oxyfuel combustion, in which the fuel is burned in oxygen instead of air. The flue gas consists of mainly CO<sub>2</sub> and water, the latter of which is condensed through cooling simplifying the CO<sub>2</sub> removal.

An alternate method, currently under intense research and development, is based on chemical looping technology which use a metal oxide as a solid oxygen carrier [4]. Metal oxide particles react with fuel, producing solid metal particles and a mixture of CO<sub>2</sub> and water. The water is condensed, leaving pure CO<sub>2</sub>. The solid metal particles are oxidized with air, producing heat and regenerating metal oxide particles that are recirculated to the combustor. An option of the chemical looping technology is the calcium looping method, which uses the alternating carbonation and then calcination of a calcium oxide-based carrier as a means of capturing CO<sub>2</sub> [4].

Key research topics addressed in our group referred to the advanced energy conversion processes integrated with CCUS with the following targets:

- Analyzing the innovative energy conversion processes with CCUS based on combustion, gasification and catalytic reforming processes for poly-generation of different total or partial decarbonized energy vectors (power, hydrogen, steam, SNG, liquid fuels by Fischer-Tropsch synthesis);
- Potential usage of renewable energy sources (biomass of various sorts, e.g. sawdust, agricultural wastes) and solid waste with energy value in poly-generation scheme in addition to the solid fossil fuel (coal and lignite);
- Advanced carbon capture methods based on gas-liquid absorption (pre- and post-combustion configurations), membrane and chemical / calcium looping systems for reducing energy penalty and capital / operational costs associated with carbon capture step;
- Evaluation of plant flexibility for better match with instant grid energy demand variations, power plant and carbon capture unit part-load operation, increasing the overall energy efficiency by better mass and thermal integration of the processes (e.g. heat and power integration studies);
- Experimental evaluations and modeling & simulation analysis of advanced energy conversion systems with carbon capture, utilization and storage to be applied for decarbonization of various industrial processes;
- Evaluation of techno-economic and environmental impact of decarbonization process to various industrial systems (e.g. heat and power generation, iron and steel, cement, various chemical industrial processes etc.).

- [1] European Commission, A policy framework for climate and energy in the period from 2020 to 2030, COM(2014) 15 final, Brussels, Belgium, 2014.
- [2] European Commission, The European Green Deal, COM(2019) 640 final, Brussels, Belgium, 2019.
- [3] Metz B., Davidson O., de Coninck H., Loos M., Meyer L., Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change (IPCC), Geneva, Switzerland, 2005.
- [4] Fan L.S., Chemical looping systems for fossil energy conversions, Wiley-AIChE, Hoboken, New Jersey, USA, 2010.

## Untang(o)ling Alzheimer's Disease

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Misfolding and aggregation of tau protein are closely associated with the onset and progression of Alzheimer's Disease. By interrogating IgG+ memory B cells from asymptomatic donors with tau peptides, we have identified somatically mutated anti-tau antibodies. One of these, CBTAU-27.1, binds to the aggregation motif in the R3 repeat domain and blocks the aggregation of tau into paired helical filaments (PHFs) by sequestering monomeric tau. A second antibody, CBTAU-28.1, binds to the N-terminal insert region and inhibits the spreading of tau seeds and mediates the uptake of tau aggregates into microglia by binding PHFs. A third antibody CBTAU-22.1 binds PHF and thus inhibits their further self-propagation. Crystal structures revealed that the combination of VH5-51 and VL4-1 recognizes a common Pro-Xn-Lys motif driven by germline-encoded hotspot interactions while the specificity and thereby functionality of the antibodies are defined by the CDR3 regions. Affinity improvement led to improvement in functionality, identifying their epitopes as new targets for therapy and prevention of AD.

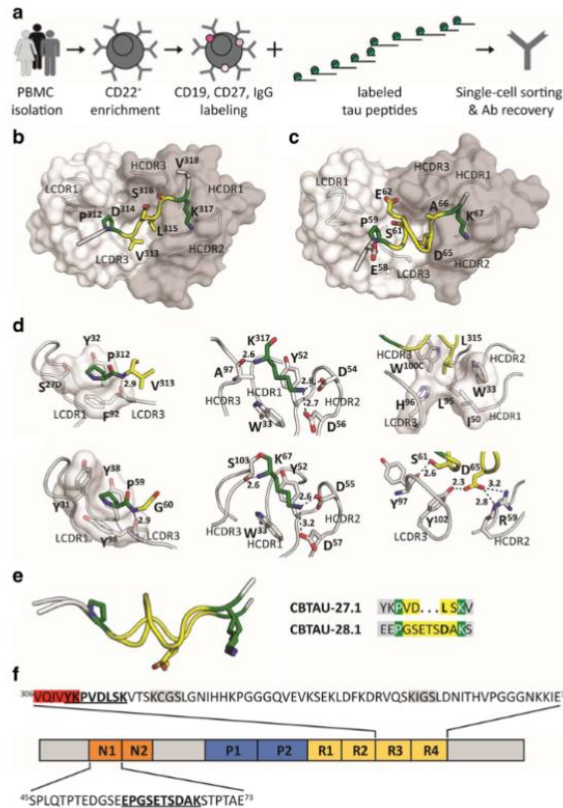


Fig. 1 Recovery and structural characterization of naturally occurring monoclonal antibodies to unphosphorylated tau epitopes from asymptomatic individuals. (a) BSelex method used to recover tau-specific memory B cells. Crystal structure of Fab CBTAU-27.1 (b) and Fab CBTAU-28.1 (c) with tau peptides A8119 and A7731, respectively. (d) Key interacting residues are plotted as sticks, polar interactions are indicated with dotted lines, and the corresponding distances are indicated in Å. (e) Structural basis for recognition of the Pro-Xn-Lys epitope motif. Epitopes of CBTAU-27.1 and CBTAU-28.1 are superimposed by aligning on the proline and lysine residues. (f) Schematic representation of tau isoform 2N4R showing the epitopes of CBTAU-27.1 and CBTAU-28.1 and the surrounding sequences.

#### References:

- Apetri et al. *Acta Neuropathologica Commun.* (2018) 6:43, 3-17  
 Van Ameijde et al, *Acta Neuropathol Commun.* (2018) 12:6(1), 59-66  
 Pascual et al., *Acta Neuropathol.* (2017) 133(5), 767-783



*ORAL PRESENTATIONS*  
Chemistry & Chemical Engineering



## Excited state processes in a molecular photoswitch

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Photochromism is a reversible transformation of a chemical species induced by electromagnetic radiation. Photoswitches are special photochromic compounds in which the product of the forward reaction remains thermally stable, the back reaction is only induced by irradiation with light. Their applications as optical sensors, memories and drug carriers open new dimensions in material and medical sciences (photopharmacology).<sup>[1]</sup>

During my research I was studying the photophysical and photochemical properties of a molecular photoswitch named 7-diethylamino-4-methyl-coumarine-3-yl-vinyl-methylpyridine-1-ium (BMG-372). This compound, upon irradiation with green light, transforms into the less stable, yellow cis isomer, and transforms back into the more stable orange trans isomer if irradiated with UV-light. BMG-372 is a new compound synthesized at the Research Centre for Natural Sciences.

As the two isomers differ in color, the photoisomerization can be monitored by UV-Vis absorption spectroscopy in both directions. From our experiments with fluorescence spectroscopy, we have concluded that while the trans isomer is a strong fluorophore, emission from the cis form cannot be observed.

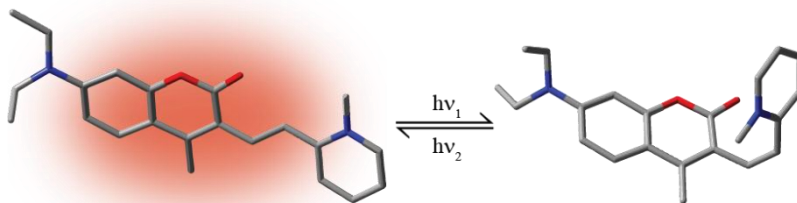


Fig. 1: Chemical structures of the isomers of the studied photoswitch, BMG-372

The excited state processes were investigated by chemical actinometry and measurement of the fluorescence quantum yield. My results were compared to quantum chemical calculations carried out at our department. These calculations confirmed the low probability of a thermally induced back reaction and the thermal stability of the cis product. Structure of both isomers were investigated and verified by NMR spectroscopy.

# Induced Magnetic Field in Carbon Nanorings: In-Plane Aromaticity/Antiaromaticity of [3]-[6]Cycloparaphenylenes

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Since 2008, [n]Cycloparaphenylenes ([n]CPPs, the smallest sidewall of single-walled armchair carbon nanotubes) and related structures burst into the scene of curved polycyclic hydrocarbons via three pivotal and elegant synthetic strategies, independently conceived by Jasti, Itami and Yamago.<sup>[1]</sup> Beyond their aesthetic structures, [n]CPPs show unique and tunable opto-electronic and host-guest properties, features that are closely related to their end-free bended  $\pi$  system. In terms of practical applications, CPPs are known as important players in material science, supramolecular chemistry, and organic electronic devices.<sup>[2]</sup>

In [n]CPPs, the  $\pi$  orbitals are oriented towards the interior of the molecular ring, which suggests a possible in-plane aromatic/antiaromatic character. However, it has been shown that synthesized [n]CPPs ( $n \geq 5$ ) are globally non-aromatic, while [4]CPP is slightly antiaromatic.<sup>[3]</sup> Interestingly, in-plane aromaticity can be turned-on by double oxidation or reduction of the nanohoops.<sup>[4]</sup> Although odd [n]CPPs dianion and dication species have  $[4m]$   $\pi$ -electrons, they possess a strong aromatic character, apparently violating Hückel's rule, while even analogues with  $[4m+2]$   $\pi$ -electrons obey Hückel's rule. This paradox was apparently resolved by considering that [n]CPPs<sup>2+</sup> sustain an aromatic ring current like that of dicationic all-*cis*-annulenes with  $[4(n-1) + 2]$   $\pi$ -electrons contributing to the global ring current.<sup>[4]</sup>

Herein, by examining the magnetic response of [n]CPPs, we argue that the similarities between the aromatic strength of all-*cis*-annulene<sup>2+</sup> and [n]CPP<sup>2+</sup> is only a matter of coincidence and in-plane aromaticity of CPP dianions and dications cannot be explain by Hückel's rule. Moreover, we

demonstrate that the increasing quinoidal character as  $n$  decreases cannot be related with the

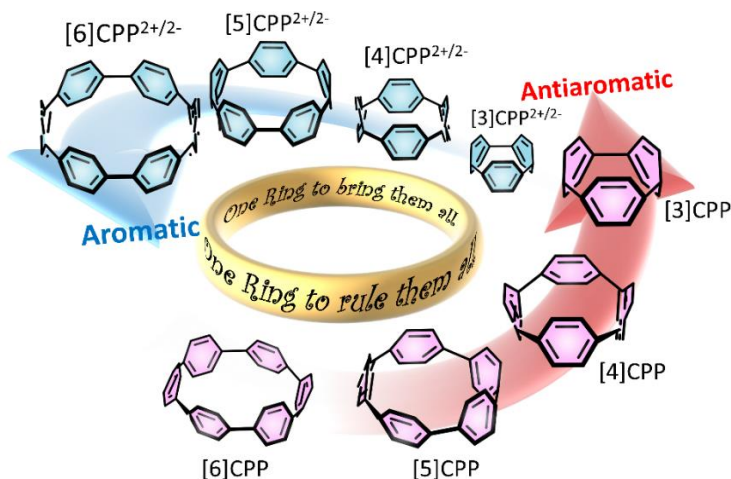


Fig. 1: Antiaromaticity/Aromaticity trend for neutral, dicationic and dianionic [3]-[6]CPPs.

the aromaticity trend in  $[n]\text{CPP}^{2+/2-}$  series (Fig 1). Furthermore, we extend the study to radical anion and radical cation species to explain, from the viewpoint of aromaticity, their lower stability than those of doubly oxidized/reduced counterparts.

Noteworthy, in the context of non-aromatic first triplet state ( $T_1$ ) of CPPs ( $n \geq 6$ ),<sup>[5]</sup> we found that [4] and [5]CPP are aromatic in their  $T_1$  state, underling the importance of smaller CPPs in spintronics and organic electronics.

Finally, we studied the local (anti)aromaticity of the phenylene rings (the building blocks of nano hoops), pointing out the tug-of-war between global in-plane antiaromaticity and local out-of-plane aromaticity especially in the case of neutral [3] and [4]CPP.

- [1] D. Wu, W. Cheng, X. Ban, J. Xia, *Asian J. Org. Chem.* **2018**, 7, 2161–2181.
- [2] E. J. Leonhardt, R. Jasti, *Nat Rev Chem* **2019**, 3, 672–686.
- [3] Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara, S. Yamago, *J. Org. Chem.* **2016**, 81, 3356–3363.
- [4] N. Toriumi, A. Muranaka, E. Kayahara, S. Yamago, M. Uchiyama, *J. Am. Chem. Soc.* **2015**, 137, 82–85.
- [5] R. Ayub, O. El Bakouri, J. R. Smith, K. Jorner, H. Ottosson, *J. Phys. Chem. A* **2021**, 125, 570–584.

## Design of sulfur-based pincer-type ligands for the stabilization of metallylenes

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Metallylenes, the divalent species of group 14 elements, have been intensively studied in the last few decades.<sup>[1]</sup> Although several types of organic ligands with steric and electronic stabilization effect were used to isolate metallylenes, only a few examples are known with pincer-type ligands.<sup>[2]</sup> In these compounds, the stabilization of the low-valent group 14 element is realized by intramolecular coordination of the ligand. The main features of these pincer-type ligands are the possibility of modifying the nature of the donor group, the length of the arm, and the substituents on the aromatic ring, thus modifying their properties.<sup>[3]</sup>

Considering these, new sulfur-based pincer-type ligands were prepared, taking into account the steric and electronic as well as the *ortho*-director effect of the sulfonyl or sulfinyl-groups.<sup>[4]</sup>

We present in this communication the synthesis of new sulfur-based pincer-type ligands and the study of the selectivity of the deprotonation reaction used for the preparation of the corresponding metallylenes (Figure 1).

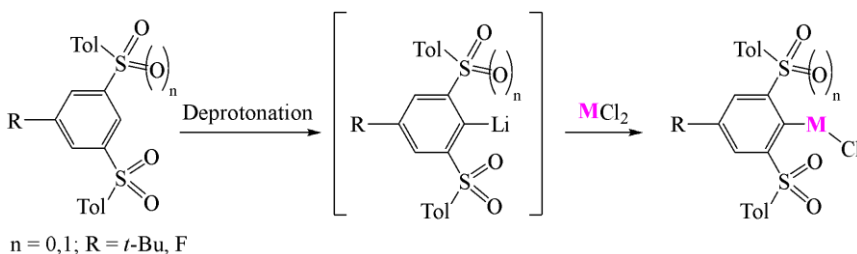


Fig. 1: New sulfur-based pincer-type ligands for the stabilization of metallylenes.

In particular, we will focus on the insertion of a fluorine atom as NMR probe, or on the insertion of a stereogenic information by means of a sulfoxide function.

*Acknowledgment:* The authors would like to thank the Centre National de la Recherche Scientifique (CNRS), the Université de Toulouse (UPS) and Research Center on Fundamentale and Applied Heterochemistry METALOMICA, Faculty of Chemistry and Chemical Engineering Cluj-Napoca.

- [1] Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.*, **2009**, *109*, 3479.
- [2] N. Deak, D. Madec, G. Nemes, G. *Eur. J. Inorg. Chem.*, **2020**, *29*, 2769.
- [3] G. van Koten, *Top. Organomet. Chem.*, **2013**, *40*, 1.
- [4] (a) M. El Ezzi, R. Lenk, D. Madec, J. M. Sotiropoulos, S. Mallet-Ladeira, A. Castel, *Angew. Chem, Int. Ed.* **2015**, *54*, 805. (b) N. Deak, O. Thillaye du Boullay, I.-T. Moraru, S. Mallet-Ladeira, D. Madec, G. Nemes, *Dalton Trans.*, **2019**, *48*, 2399.



# Organoselenium compounds – synthesis and structural characterization

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Organoselenium chemistry has attracted interest due to the fact that selenium-containing compounds have shown significant applications in different fields of science such as organic synthesis, biology and material science.<sup>[1]</sup> Organoselenium compounds containing nitrogen and/or oxygen donor atoms incorporated within the organic groups attached to the selenium atoms show a constantly interest owing to their successful use in coordination chemistry, as neutral or ionic ligands towards transition metals, being able to stabilize metal complexes with promising optical properties.<sup>[2]</sup>

Our recent interest was focused on the preparation, structural characterization, and reactivity of  $[2-\{2-C_6H_5-(4H)\text{-oxazol-5-one}\}C_6H_4]_2Se_2$  (Figure 1) and related compounds.

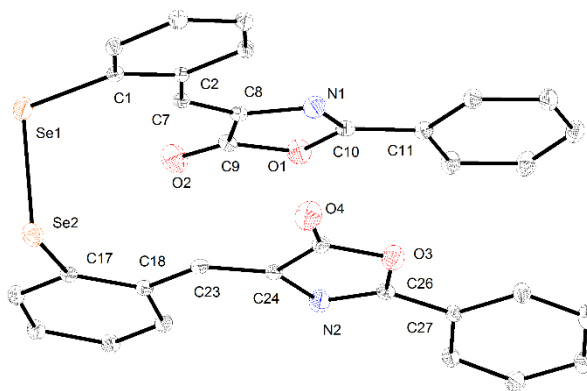


Fig. 1: Molecular structure of  $[2-\{2-C_6H_5-(4H)\text{-oxazol-5-one}\}C_6H_4]_2Se_2$ .

For the identification and characterization of the compounds multinuclear NMR ( $^1H$ ,  $^{13}C\{^1H\}$ ,  $^{77}Se\{^1H\}$ ) spectroscopy, IR spectroscopy,

elemental analysis, mass spectrometry and single-crystal X-ray diffraction were used, when appropriate. UV-Vis absorption spectra were recorded to investigate the optical properties.

- [1] J. Mukherjee, S. S. Zade, H. B. Singh, R. B. Suno, *Chem. Rev.*, **2010**, *110*, 4357.
- [2] S. Panda, A. Panda, S. S. Zade, *Coord. Chem. Rev.*, **2015**, *300*, 86.

## **Dynamic modeling of CO<sub>2</sub> capture using intercooled absorber column**

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Climate change has a direct impact on human life, due to the greenhouse gas emissions, carbon dioxide is accounting for about 77% of all greenhouse gas emissions in the atmosphere. The concentration of carbon dioxide in the atmosphere has risen considerably in the last decades, from about 320 ppm to almost 410 ppm in 2019, this increase is mainly due to the burning of fossil fuels in power plants, iron and cement production, and also due to the massive cutting of forests and vegetations.<sup>[1]</sup>

One of the most suitable solutions to reduce the amount of CO<sub>2</sub> release into the atmosphere from anthropogenic sources (e.g., coal-fired power plants, cement and steel production, oil refineries, etc.) is the Carbon Capture, Utilization and Storage technique (CCUS). The gas-liquid absorption process is one of the most mature, efficient, and attractive technology for CO<sub>2</sub> capture, due to the high separation efficiency (over 90%), and low cost.<sup>[2]</sup>

The chemical reaction between CO<sub>2</sub> and MEA is exothermal, so during the absorption process, the temperature of the liquid phase will increase, which will amplify the MEA and water evaporation, having a negative impact on the environment and also on the efficiency of CO<sub>2</sub> absorption. In order to minimize the loss of MEA through vaporization and increase the CO<sub>2</sub> capture rate, the use of an absorption column with intercooling after each layer of packing material is employed. A schematic representation of the CO<sub>2</sub> capture process using intercooled absorber column is represented in Fig. 1.

The inlet flue gas flows into the absorption column and enters at the bottom of the first layer of packing material, the MEA solution is introduced at the top of the column, after each layer, the liquid solution is extracted in order to be cooled and afterwards is introduced at the top of the next layer of packing material. Over the length of the column the CO<sub>2</sub> is absorbed in the MEA solution, and the clean gas is evacuated at the top of the column.

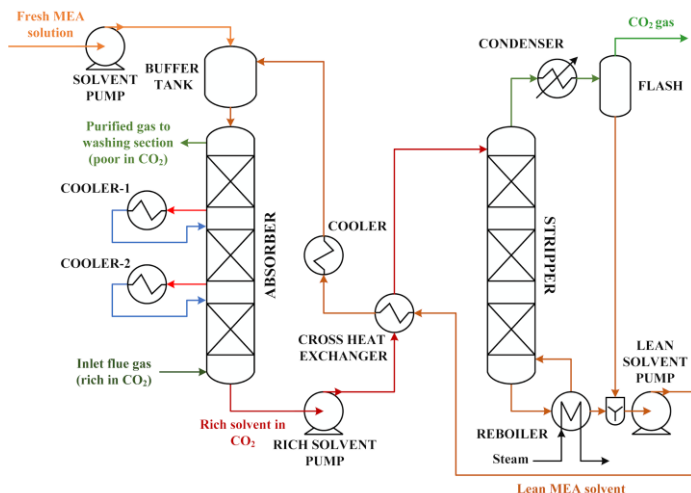


Fig. 1: Flowsheet configuration of CO<sub>2</sub> capture using intercooled absorber

In this work, a comprehensive dynamic mathematical model for CO<sub>2</sub> capture process using intercooled absorber column is developed. The dynamic mathematical model was implemented in Matlab/Simulink and validated with experimental data from literature. The model contains partial differential equations that are describing the total mass, component and energy balance of liquid and gas phases, for each layer of packing material.

The developed dynamic mathematical model will be used to evaluate CO<sub>2</sub> capture rate and temperature variation over the length of the packing layers of material, and also to predict with accuracy other process parameters, such as gas and liquid flow rates and compositions, mass transfer coefficients, velocity profiles, etc. By comparing the simulation results of the intercooled absorber with a classic one, we observe a better absorption rate and a decrease in the solvent evaporation. The model will also be used to establish the process parameters under flexible operation conditions, in order to determine the system response in time for different scenarios.

**Acknowledgment:** This work was supported by a one-year scholarship granted by the World Federation of Scientists.

- [1] F. Nocito, A. Dibenedetto, *Curr. Opin. Green Sustain. Chem.* **2020**, 21, 34–43.
- [2] W. H. Tay, K. K. Lau, L. S. Lai, A. M. Shariff, T. Wang, *J. Nat. Gas Eng.* **2019**, 71, 102977.

# Synthesis and structural characterization of new diorganoselenides and their silver(I) complexes. Antiproliferative activity assay.

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Selenium is an essential trace element that has been extensively used in developing new organoselenium compounds that can act as neutral ligands towards various transitional metals.<sup>[1,2]</sup> The metal complexes found applications in organic synthesis, materials science or as biologically active species with antioxidant, chemopreventive, anticancer or cytotoxic capabilities.<sup>[3,4]</sup> It was observed that the specific properties of hypercoordinated organoselenium compounds are enhanced due to the organic groups bearing donor atoms capable of intramolecular N→Se interactions.<sup>[2]</sup> In addition, ligands with thiazole groups raised over time an increased attention due to their coordination ability and the expected improved biological properties.<sup>[5]</sup>

We report here on the synthesis and structural characterization of a series of novel silver(I) complexes of the neutral ligands bearing thiazole functionalities, namely  $\text{Se}(\text{CH}_2\text{Phtz})_2$  (**1**) and  $[2-\{\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]\text{Se}(\text{CH}_2\text{Phtz})$  (**6**) (Phtz = phenylthiazole). The homoleptic diorganoselenide **1** was obtained by reacting  $\text{Na}_2\text{Se}$  and 4-chloromethyl-2-phenylthiazole in a 1:2 molar ratio. The heteroleptic ligand **6** was obtained by reducing  $[2-\{\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]_2\text{Se}_2$  with  $\text{NaBH}_4$  followed by the reaction with 4-chloromethyl-2-phenylthiazole.<sup>[6]</sup>

The metal complexes were synthesized by reacting **1** and **6** with  $\text{AgNO}_3$ ,  $\text{AgOTf}$  ( $\text{OTf} = \text{CF}_3\text{SO}_3$ ) and  $\text{AgClO}_4$ , as appropriate.

The new compounds were investigated by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{77}\text{Se}$  and  $^{19}\text{F}$ , as appropriate), ESI+ mass spectrometry, IR spectroscopy and molar conductivity, and single-crystal X-ray diffraction. The silver(I) complexes **2-4** exhibit antiproliferative activity against murine melanoma B16.F10 cells.

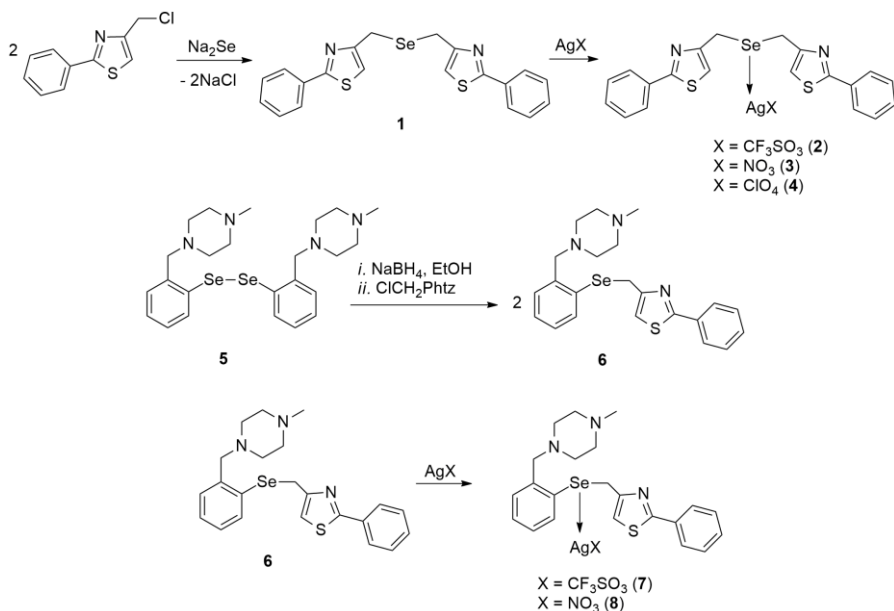


Fig. 1: Synthesis of compounds **1-8**.

- [1] E. S. J. Arnér, *Exp. Cell Res.* **2010**, 316(8), 1296;  
 [2] A. J. Mukherjee, S. S. Zade, H. B. Singh, R. B. Sunoj, *Chem. Rev.* **2010**, 110, 4357.  
 [3] B. Banerjee, M. Koketsu, *Coord. Chem. Rev.* **2017**, 339, 104.  
 [4] G. Mugesh, H. B. Singh, *Chem. Soc. Rev.* **2000**, 29, 347.  
 [5] A. M. Vijesh, A. M. Isloor, P. Shetty, S. Sundershan, H. K. Fun, *Eur. J. Med. Chem.* **2013**, 62, 410.  
 [6] M. Kulcsar, A. Beleaga, C. Silvestru, A. Nicolescu, C. Deleanu, C. Todasca, A. Silvestru, *Dalton Trans.* **2007**, 21, 2187.

## Synthesis and structural characterization of new organotin(IV) compounds with Sn-O-E bonds (E= C, Si)

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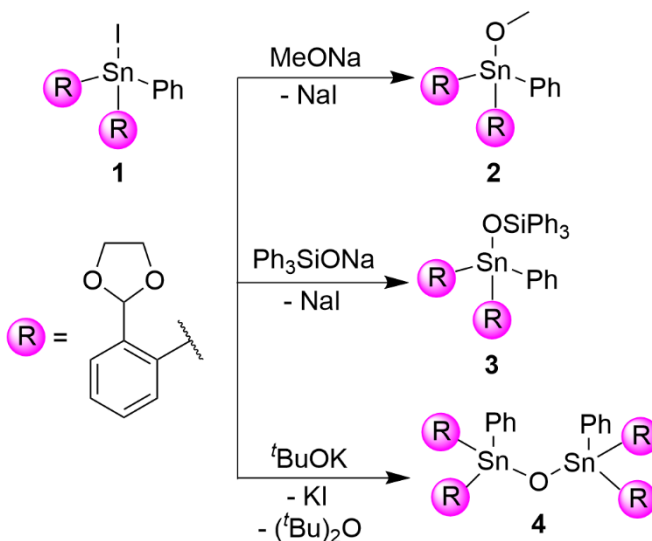
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Organotin(IV) compounds containing Sn-OR bonds (alkoxides) or Sn-OSiR<sub>3</sub> bonds (siloxides) have mostly been studied in the last 20 to 40 years. Compared to the organotin(II) derivatives, these compounds are less common and their reactivity was less investigated.

Organotin(IV) alkoxides and/or siloxides are generally obtained by reacting an organotin halide with an alkoxide of Na/K,<sup>[1]</sup> or with the Li alkoxide obtained from an alcohol and *n*-butyllithium.<sup>[2]</sup> Other methods describe *trans*-alcoholysis reactions<sup>[3]</sup> or the reaction of tin(IV) amides with lactides, following a ring opening mechanism.<sup>[4]</sup>

We report the synthesis of new triorganotin(IV) alkoxides and siloxides bearing one phenyl group and two *ortho*-substituted phenyl-1,3-dioxolane fragments as ligands. The halide [2-{(CH<sub>2</sub>O)<sub>2</sub>CH}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SnPhI (**1**) was used as the starting material in all syntheses. The organotin(IV) methoxide [2-{(CH<sub>2</sub>O)<sub>2</sub>CH}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SnPhOMe (**2**) and siloxide [2-{(CH<sub>2</sub>O)<sub>2</sub>CH}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SnPhOSiPh<sub>3</sub> (**3**) were obtained in good yields and characterized by multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn) NMR spectroscopy. The attempt to synthesize the organotin(IV) derivative with the *tert*-butoxy group led to the formation of the more stable oxide [2-{(CH<sub>2</sub>O)<sub>2</sub>CH}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SnPh]<sub>2</sub>O (**4**), bearing the Sn-O-Sn fragment. Compound **4** was characterized by multinuclear NMR spectroscopy and its identity was confirmed by elemental analysis and mass spectrometry. The Sn-O-Sn fragment will be further functionalized by reacting compound **4** with carbon dioxide to form an organotin(IV) carbonate, [2-{(CH<sub>2</sub>O)<sub>2</sub>CH}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SnPh]<sub>2</sub>CO<sub>3</sub>.

The organotin(IV) methoxide **2** is air- and moisture-sensitive and it decomposes with the formation of the oxide **4**.



Scheme 1. Synthesis of compounds 2-4.

- [1] A. G. Lichtscheidl, M. T. Janicke, B. L. Scott, A. T. Nelson, J. L. Kiplinger, *Dalton Trans.*, **2015**, 44, 16156.
- [2] S. Beaini, G. B. Deacon, M. Hilder, P. C. Junk, D. R. Turner, *Eur. J. Inorg. Chem.*, **2006**, 3434.
- [3] C. D. Chandler, J. C. Caruso, M. J. Hampden-Smith, *Polyhedron*, **1995**, 14, 2491.
- [4] M. C. Chisholm, E. E. Delbridge, *Chem. Commun.*, **2001**, 1308.



## **Antiacneic Effect of Some Cosmetic Formulations Based on *Eugenia aromaticum* and *Foeniculum vulgare* Essential Oil**

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*Propionibacterium acnes* is a bacterium that is found on the surface of human skin, especially flourishing in areas abundant in the sebaceous glands. These, whether free or attached to hair follicles, release sebum – a fatty substance (triglycerides, squalene, cholesterol, wax esters) and dead cell debris.<sup>[1]</sup>

By the accumulation of bacteria in the follicular channel that crosses the dermo-epidermal layer, it clogs it, blocking the release of the content of the sebaceous glands, which leads to the gradual inflammation of the area and the appearance of comedones - acne.<sup>[2]</sup> Both fennel (*Foeniculum vulgare*) and clove (*Eugenia aromaticum*) essential oils display an antibacterial activity against *P. acnes*, by inhibiting the inflammatory response of acne caused by the bacteria.<sup>[3,4]</sup> This work is focused on testing the properties of these essential oils, as well as the change in the antibacterial activity when used in different formulations of anti-acne facial cream.

The anti-acne activity of crude oil extracts and cosmetic formulation were tested in the presence of bacterial species *Propionibacterium acnes*, *Escherichia coli* and *Staphylococcus epidermidis* previously inoculated on a TSB medium. The plates were incubated at 37 °C for 16-20 hours in the presence of cellulose discs saturated with the sample to be analyzed. The minimum inhibitory concentration of the sample (volatile oil and cosmetic formulations) was determined for each bacterial species.

In the case of *P. acnes*, the minimum inhibitory amount of fennel oil was 5 mg, reaching a zone of inhibition of 8 mm and for 20 mg of oil the zone of inhibition was 11 mm. The cream with a high water composition (W) shows very similar results to the essential oil, without the percentage of oil in the cream significantly changing the diameter of inhibition (no. 4-6). The results show that the fat-based cream (F) is not effective for any bacteria

tested. This is most likely due to the difficult process of releasing the oil from the fat-based cream or the diffusion of this cream into the aqueous medium. A commercially available cream whose anti-acne activity is known was used as a positive control.



No.	Sample	<i>P. acnes</i> , Ø [mm]
1	5 mg fennel oil	9
2	20 mg fennel oil	11
3	40 mg fennel oil	11
4	20 mg (1% fennel oil) – F	-
5	20 mg (2% fennel oil) – F	-
6	20 mg (5% fennel oil) – F	-
7	20 mg (1% fennel oil) – W	10
8	20 mg (2% fennel oil) – W	11
9	20 mg (5% fennel oil) – W	12
10	20 mg – positive control	11

Fig. 1: The antioxidant activity plate (image- left) and the inhibition zones (table – right) of oil and different fennel formulas in the presence of *P. acnes*.

The results obtained demonstrate that the raw fennel oil extract as well as cosmetic formulas exhibit anti-acne activity in the presence of *Propionibacterium acnes*.

- [1] H. C. Williams, R. P. Dellavalle, S. Garner, *The Lancet* **2012**, 379(9813), 361.
- [2] J. J. Leyden, *Semin. Cutaneous Med. Surg.*, **2001**, 20(3), 139.
- [3] M. S. Ali-Shtayeh, Al-Assali, J. Rana, *Afr. J. Microbiol. Res.* **2013**, 7, 2560.
- [4] T. Tsai, W. Huang, T. Lien, Y. Huang, H. Chang, C. Yu, P. Tsai, *Food Agric. Immunol.* **2017**, 28:5, 916.

## Titanium Carbide MXenes functionalization for heterogenous catalysis in neutral hydrolysis of PET

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Efficient recycling of plastics, particularly polyethylene terephthalate (PET), is a growing concern in the context of our current climate and pollution problem.<sup>[1]</sup> The main problem met by the industry today is a sustainable way to get rid of plastic waste and to be able to reuse it indefinitely or at least not let it reach the environment. While laboratories around the world are working to find sustainable substitutes, a large body of research is focused on novel methods of recovering the plastics already manufactured and in use or discarded. One such method of recycling is the neutral hydrolysis of PET in a mild environment which guarantees a as low as possible ecological impact of the reaction. This way we can break down the polymer chains back into its constituents: ethylene glycol and, more importantly terephthalic acid (TPA), which can subsequently be used as raw materials for new plastic products.

PET hydrolysis, especially in a neutral medium, is a catalytic reaction and the quality of the catalyst can greatly influence its yield and required conditions, such as pressure and temperature. In this study we investigated the performance of Titanium Carbide MXenes as heterogenous catalysts in this reaction. MXenes are relatively new two-dimensional materials that envelope important properties of both metals and ceramics, such as high thermal and electrical conductivity, mechanical strength and low density. Due to their increased resistance to high temperatures and oxidation, they make perfect candidates as catalysts in all sorts of reactions.<sup>[2]</sup>

In order to obtain the 2D nanosheet structure of the  $\text{Ti}_3\text{C}_2$  MXene, we start from the precursor  $\text{Ti}_3\text{AlC}_2$  MAX phase, and we etch it with LiF and HCl to form *in situ* HF. Afterwards we deposit functional acidic groups on the material by reaction with the arenediazonium salt of sulfaniline. As confirmation of the crystalline structure and the successful activation

with sulfonated groups, SEM, TEM, XRD and FT-IR analysis were performed on the samples.

In the depolymerization reactions, three types of functionalized MXenes were tested at temperatures of 160, 170, 180°C with three distinct sources of PET: transparent bottle, green bottle and synthetic T-shirt. Our experiment shows exceptionally good yields (70%) of TPA at temperatures below 180°C.

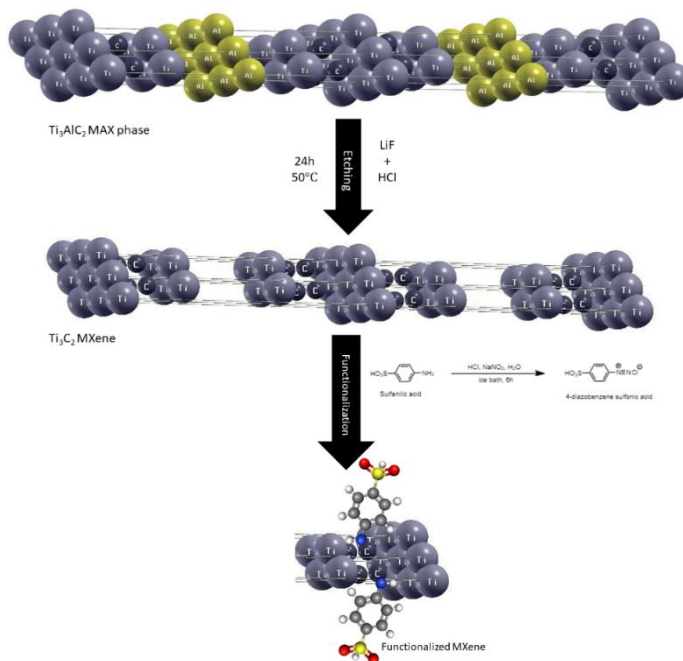


Figure SEQ Figure \\* ARABIC 1: Synthesis of functionalized MXene

- [1] R. Geyer, „Production, use, and fate of synthetic polymers,” in *Plastic waste and recycling*, Elsevier, **2020**, pp. 13-32.
- [2] A. Morales-Garcia, F. Calle-Vallejo și F. Illas, „MXenes: new horizons in catalysis,” *ACS Catal.* **2020**.

## **Solid phase-FDC1 - activity assay based on fluorescent detection of styrenes**

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A large number of mutant enzyme variants obtained by directed mutagenesis require a rapid and qualitative activities test before HPLC methods, which are sometimes too particular or of limited throughput.

Therefore, a quick detection method of the product using whole cells as a biocatalyst is increasingly used in order to avoid the tedious isolation of each enzyme variant. Such methods by using a wide range of substrates and correlated with molecular modeling data significantly reduce the working time requested within the activity screens.

The idea of this experiment is to use a method that excludes from the beginning those biocatalysts that are inefficient in the decarboxylation reaction of various cinnamic acids <sup>[1]</sup>. The purpose of our research is to monitor the formation of styrene derivatives following their reaction with a tetrazole fluoroprobe, by UV type detection.

The fluorescent solid-phase assay method <sup>[2]</sup> was used to test the activity of the 23 FDC1 (ferulic acid decarboxylase from *Saccharomyces cerevisiae*) mutant enzymes on the four substrates (Fig.1). For the 4 substrates, at least one mutant variant more active than the native enzyme was identified. For example, in the case of decarboxylation of substrate 1a, the best performing biocatalyst was I398V-ScFDC1. The relative activity recorded with the native enzyme was 66%.

The results obtained from the solid phase fluorescent assay as relative activity value fluorescence signal intensities, were compared with the conversion values recorded by HPLC analysis. Most of the hits detected were supported by both HPLC-detected conversion values and molecular modeling data, that revealed the orientation of the substrates in the modified FDC1 catalytic site.

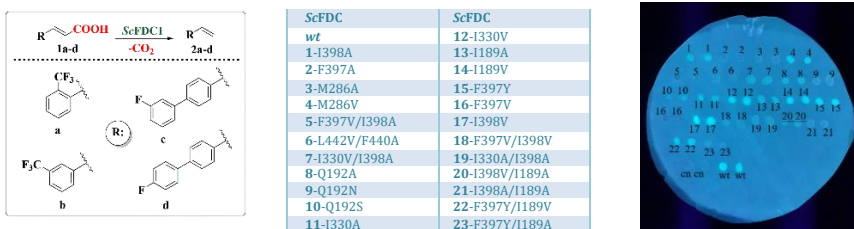


Fig. 1: Substrate panel: cinnamic acid derivatives **1a-d** (left), the ScFDC1 variant library (middle) and detection of hits with decarboxylase-activity for **1a** (right).

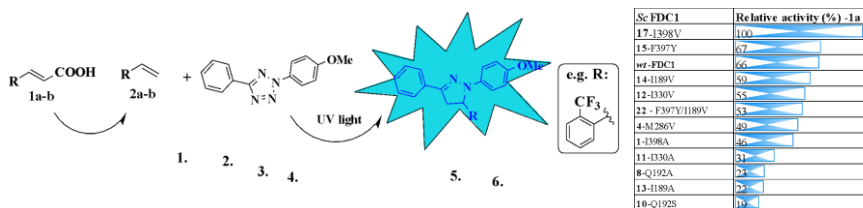


Fig. 2: Steps of the fluorescent solid-phase assay method: **1.** transfer of colonies to membrane; **2.** IPTG induced-gene expression; **3.** cell permeabilization and dialysis; **4.** decarboxylation by FDC1; **5.** fluorogenic detection of styrenes and **6.** Selection of hits with initial FDC1 relative activity (table – right) – fig. 1.

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[1] Emma Zsófia Aletta Nagy, Csaba Levente Nagy, Alina Filip, Katalin Nagy, Emese Gál, Róbert Tóth, László Poppe, Csaba Paizs, László Csaba Bencze, *Scientific reports* (2019).

[2] Horia Duță, Alina Filip, Levente Csaba Nagy, Emma Zsófia Aletta Nagy, Róbert Tóth, László Csaba Bencze: *Scientific Reports*, (2022).

## **Preliminary testing and optimization of suitable encapsulation methods and carriers for *Vaccinium* spp. bioactive compounds**

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Blueberries (*Vaccinium* spp.) have great beneficial effects, and so do their leaves that are rich in phenolics.<sup>[1]</sup> Despite this, after consumption of products containing nutraceuticals, they pass through the gastrointestinal tract, where digestive enzymes are involved in making nutrients and bioactive compounds available for absorption through the wall of the small intestine.<sup>[2,3]</sup>

Thus, gastrointestinal digestion can influence structural changes that affect the stability and bioaccessibility of the phytochemicals present in the food matrix. In the case of blueberry leaves, following analysis and interpretation of data obtained as a result of research work for the bachelor's thesis, it was found that the bioaccessibility of both polyphenols and antioxidant compounds from blueberry leaves decreased drastically along the gastrointestinal tract. In this regard, technologies involving encapsulation of these compounds have been developed with the aim of modifying their physical properties in order to eliminate the shortcomings leading to low bioaccessibility.<sup>[4,5]</sup>

The main aim of the current work is to test the efficacy of lecithin as an encapsulation carrier for the bioactive compounds extracted from blueberry leaves and optimize the fabrication of blueberry leaves extract-loaded nanoliposomes.

For the optimization of the encapsulation process, different concentrations of phenolic compounds (500, 1,000, and 1,500 ppm) of blueberry leaves extract and lecithin (0.5, 1.25, and 2% w/w) were applied at different process temperatures (30, 50, and 70°C). Figure 1 shows the method employed for obtaining the loaded nanoliposomes.

In order to analyze the entrapment efficiency, the phenolic content was determined using the Folin–Ciocalteu method and after that, the efficiency was calculated using the following equation:

$$EE\% = \left( \frac{P_i - P_s}{P_i} \right) \cdot 100$$

where  $P_i$  is the total amount of phenolic compounds and  $P_s$  represents the free phenolic compounds in the supernatant.

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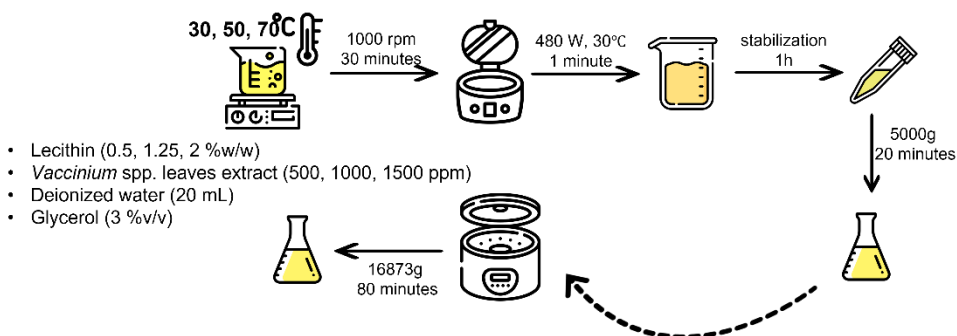


Fig. 1: Fabrication of blueberry leaves extract-loaded nanoliposomes.

- [1] H. Wua, Z. Chaia, R. P. Hutabarata, Q. Zengb, L. Niua, D. Lia, H. Yub, W. Huang; *Food Res. Int.* **2019**, 122, 548.
- [2] Y. Sidorova, V. Shipelin, V. Mazo, S. Zorin, N. Petrov, A. Kochetkova; *Nutrition*, **2017**, 41, 107.
- [3] A. Cilla, A. González-Sarrías, F. A. Tomás-Barberán, J. C. Espín, R. Barberá; *Food Chemistry*, **2009**, 114, 813.
- [4] M. Peanparkdee, S. Iwamoto; *Food Reviews International*, **2022**, 38, 335.
- [5] P. Vos, M. M. Faas, M. Spasojevic, J. Sikkema; *International Dairy Journal*, **2010**, 20, 292.



## **Functionalized mesoporous silica nanoparticles as carriers for natural compounds used for topical applications**

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In the last two decades, mesoporous silica nanoparticles (MSNs) have attracted researchers' attention as potential carriers in drug delivery applications, along with liposomes, dendrimers, lipids, and polymeric nanoparticles.<sup>[1]</sup> MSNs show specific properties like high pore volume and specific surface area being able to host a large amount of cargo molecules, high content of silanol groups, which allow chemical reactions for MSNs surface functionalization, good biocompatibility, chemical stability, etc.<sup>[1,2]</sup>

The MSNs surface can be modified with various organic moieties that allow acid-base or hydrogen bonding interactions between cargo molecules (active pharmaceutical ingredients or natural compounds) and carrier that can be tailored function of the purpose. The MSNs surface modification can be performed by two approaches, co-condensation and post-synthesis functionalization. Also, the MSN surface properties can be modified by deposition of inorganic nanoparticles either on their external or pore walls surface.

Due to the widespread and continuous use of antibiotics, bacteria are becoming resistant to them.<sup>[3]</sup> To overcome this resistance, in recent years special attention has been given to natural compounds extracted from plants with antibacterial potential. Nanotechnology could also contribute to this, for instance by using MSNs in the delivery of antibacterial agents. Moreover, MSNs can be modified with inorganic nanoparticles like Ag or ZnO that exhibit their antimicrobial activity and hence, a synergistic effect can be achieved.

Herein we present the synthesis and characterization of various functionalized MCM-41-type silica nanoparticles either with organic

groups (mercaptopropyl, cyanopropyl, propionic acid and ethylenediamine) or inorganic nanoparticles (Ag or ZnO) that were further used as supports for natural compounds extracted from vegetal material. The loading of the polyphenolic extract was carried out through incipient wetness impregnation method followed by vacuum drying.

The prepared materials were investigated by various techniques: small and wide-angle X-ray diffraction, Fourier Transform infrared spectroscopy, thermal analysis, N<sub>2</sub> adsorption/desorption isotherms recorded at 77 K, and scanning electron microscopy (SEM).

The analysis showed that the materials possess high pore volume and specific surface area, an evenly distribution of the moieties and high pore loading with the natural extract. Those conclusions suggest the possibility of using those composite materials in medicine.

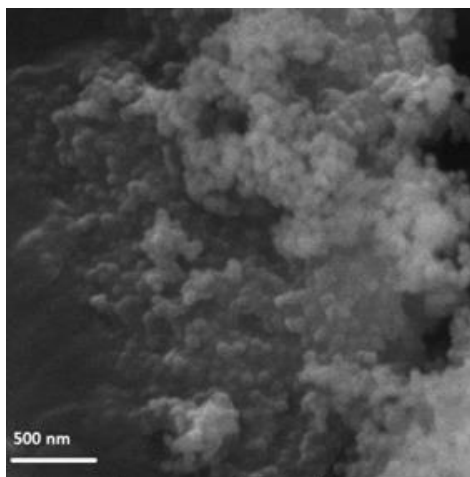


Fig. 1: SEM image of MCM-41 functionalized with mercaptopropyl groups by co-condensation approach.

## References

- [1] K. A. Aitah, W. Lojkowski, *Pharmaceutics*, **2021**, *13*, 143.
- [2] M. Manzano, M. Vallet-Regi, *Adv. Funct. Mater.*, **2020**, *30*, 2.
- [3] R. R. Castillo, M. Vallet-Regi, *Int. J. Nanomed.*, **2021**, *16*, 4409-4430.

## **The influence of chemical interface damping in the dehalogenation of 4-chlorothiophenol and 4-bromothiophenol adsorbed on silver nanoparticles**

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Chemical reactions dictate every process in our daily lives both from nature's standpoint as well as at an industrial level. This study examines the correlation between the chemical interface damping and the dehalogenation reaction rate by using surface-enhanced Raman scattering and dark field scattering.

In order to quantify the chemical interface damping, the study conducted several dark field scattering measurements at single particle level on 4-chlorothiophenol (CTP) and 4-bromothiophenol (BTP) molecules adsorbed on silver nanoparticles. From the resulting spectra we have calculated the C factor which describes the rate of energy transfer from the plasmon resonance to the adsorbate.

The reaction rate constant has been calculated from several time-series acquired through surface-enhanced Raman scattering measurements using different laser powers. From analyzing the measurements, we can observe that the dissociation rate of the thiol-halogen bond increases with the laser power, implying the creation of more hot carriers through plasmonic resonance, which when transferred to the adsorbate induce the bond breaking.

Finally, the study correlated the chemical interface damping with the reaction rate by comparing the constants C and k for CTP and BTP. The results showed that the nanoparticles-adsorbate complex containing BTP has a higher rate of energy transfer than the one with CTP,  $C_{BTP} > C_{CTP}$ . Additionally, the reaction rate for BTP is higher than that of CTP,  $k_{BTP} > k_{CTP}$ . Therefore, the study concludes that there is a positive correlation between chemical interface damping and the reaction rate, with higher chemical interface damping resulting in higher rates of reaction.

## References

- [1] A. Stefancu, O.M. Biro, O.Todor-Boer, I. Botiz, E. Cortes, N. Leopold, *Halide-Metal Complexes at Plasmonic Interfaces Create New Decay Pathways for Plasmons and Excited Molecules*, ACS Photonics, **2022**, 9 (3), 895-904.
- [2] E. Cortes, *Activating plasmonic chemistry*, Science, **2018**, 362 (6410), 28-29.
- [3] A. Stefancu, S.D. Iancu, L. Leopold, N. Leopold, *Contribution of chemical interface damping to the shift of surface plasmon resonance energy of gold nanoparticles*, Rom. Rep. Phys., **2020**, 72, 402, 1-12.

# Kinetic studies on the gas-phase reaction of OH radical with *p*-tolualdehyde

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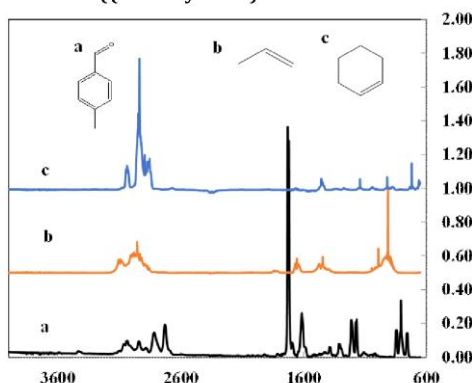


Fig.1: The gas-phase IR spectra for *p*-tolualdehyde (a), and the two reference compounds, propene (b) and cyclohexene (c)

The aromatic OVOCs represent a class of hydrocarbons, mostly released into the atmosphere as the aftermath of human activity. However, aromatic OVOCs can also reach the atmosphere as constituents of biomass burning and wildfire events, more frequent in the last decade as a consequence of global warming and climate change.<sup>[1]</sup>

Tolualdehydes were identified in the urban atmosphere as primary pollutants, emitted by industrial processes and secondary pollutants, as gas phase products from reactions of aromatic hydrocarbons with tropospheric radicals. Atmospheric degradation processes of *p*-tolualdehyde lead to the formation of photooxidants and secondary organic

aerosols (SOA).<sup>[2,4]</sup> The daytime gas-phase removal processes of *p*-tolualdehyde are mainly represented by reactions with OH radicals or direct sunlight photodegradation.<sup>[2,3]</sup>

In this research study, the gas-phase kinetic rate coefficient for the reaction of *p*-tolualdehyde initiated by OH radicals was determined under simulated atmospheric conditions. The investigations were performed using the Environmental Simulation Chamber made of quartz from University “Alexandru Ioan Cuza” (ESC-Q-UAIC) from Iasi. The ESC-Q-UAIC reaction chamber, a cylindrical quartz-made reactor with a volume of 760 L, is connected to a long-path FT-IR spectrometer. An external White type multiple reflection optical system ensures a total path-length of  $(492 \pm 1)$  m inside the chamber. OH radicals were produced *in situ* by photolysis of methyl nitrite at  $\lambda_{\text{max}} = 365$  nm. The rate coefficient has been obtained by using a relative kinetic technique with propene and cyclohexene as reference compounds. Prior to the experimental investigations, possible interferences due to wall losses and photolysis have been investigated.

For the reaction of *p*-tolualdehyde initiated by OH radicals, an average rate coefficient value of  $(1.51 \pm 0.26) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was obtained. The present study would evaluate the atmospheric lifetime of *p*-tolualdehyde in the atmosphere and compare the experimental results with the rate coefficient obtained from the stability-activity relationship approach. Possible implications of the present work in computational and modeling studies are also discussed.

**Acknowledgement:** The study was carried out with the financial support provided by the project PN-III-P2-2.1-PED2021-4119 (SOA-REACTOR) from UEFISCDI. Also, recognition is given to the RECENT AIR project under the MySMIS grant agreement no. 127324.

[1] Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J., and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, London, 2002.

[2] Calvert, J.G., Mellouki, A., Orlando, J.J., Pilling, M.J., and Wallington, T.J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, 2011.

[3] Clifford, G.M.; Hadj-Aïssa, A-H.; Healy, R.M.; Mellouki, A.; Muñoz, A.; Wirtz, K.; Reviejo, M-M.; Borrás, E.; Wenger, J-C.; The Atmospheric Photolysis of *o*-Tolualdehyde. Environmental Science & Technology, **45** (22), 9649-9657, (2011).

# Production and activity assessment of the recombinant PET-degrading LC cutinase

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Nowadays one of the main environmental problems is plastic pollution. The presence of large-scale environmental waste requires an increasingly urgent solution for its decomposition.<sup>[1]</sup> Environmentally friendly organic waste degradation approaches, fulfilling the requirements of green chemistry has been emerged over the last few years.<sup>[2]</sup> Among them, enzymatic plastic degradation procedures, especially those targeting the disintegration of polyethylene terephthalate (PET) into its monomers: BHET, MHET, TPA and EG using hydrolases and cutinases have been recently explored. These enzymes gained high interest, providing significant advances in the plastic recycling technologies and became new target biocatalysts.<sup>[3]</sup>

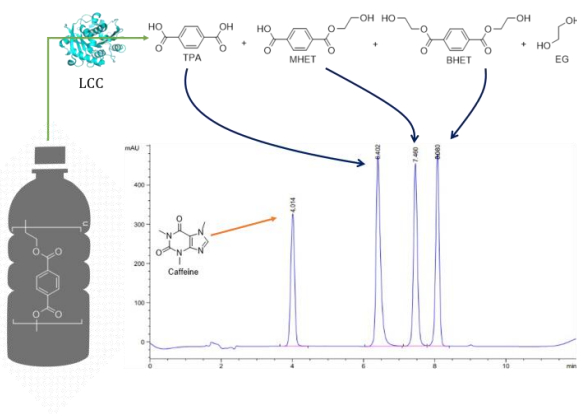


Fig. 1: HPLC analysis of the biodegradation products (TPA at 6.4 min, MHET at 7.8 min and BHET at 8 min) of PET using caffeine (at 4 min) as internal standard.

Within the design and development of an efficient PET-degrading biocatalyst, an efficient recombinant expression system for the production

of the enzyme and a precise enzyme activity assay (of high sensitivity, specificity, and reproducibility) are required. During our experiments, we developed an efficient expression system (testing different expression vectors – pET-28a(+), pET-15b, pET-21a(+)) and host cells –*E.coli* Rosetta pLysS, Rosetta-gami B, BL21 Gold, ArcticExpress) to produce one of the most efficient PET degrading enzymes, the leaf branch compost cutinase (LCC).[4] Moreover, for the assessment of the catalytic efficiency, we first employed two of the existing analytical methods (based on UV-Vis spectroscopy[5] and HPLC[4] respectively) and then on account of the limitations of these methods we developed a novel HPLC-based assay of improved accuracy using caffeine as internal standard (**Fig. 1**).

Using the developed methods, we evaluated the catalytic efficiency of the recombinant biocatalysts obtained from the optimal expression system (pET-21a(+)-LCC construct in Rosetta pLysS) (**Fig 2**).

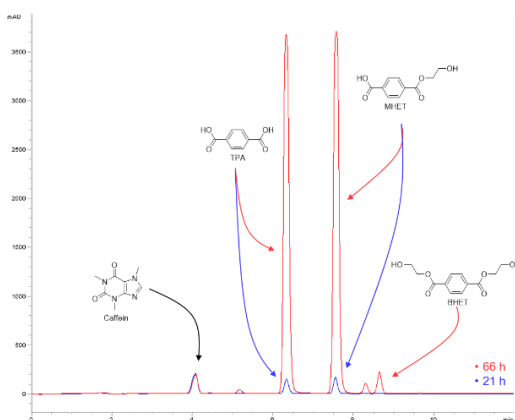


Fig. 2: Biodegradation product of the PET film after 21 (blue) and 66 (red) hours reaction time, using LCC as biocatalyst.

- [1] M. Oliveira, M. Almeida, *Trends Anal. Chem.*, **2019**, 114, 196-201.
- [2] F. Kawai, T. Kawabata, M. Oda, *ACS Sustainable Chem. Eng.*, **2020**, 8, 24, 8894.
- [3] N. A. Samak, Y. Jia, M. M. Sharshar, *Environ. Int.*, **2020**, 145, 106144,
- [4] V. Tournier, C. M. Topham, A. Gilles, B. David, C. Folgoas, E. Moya-Leclair, E. Kamionka, M. L. Desrousseaux, H. Texier, S. Gavalda, M. Cot, E. Guemard, M. Dalibey, J. Nomme, G. Cioci, S. Barbe, M. Chateau, I. Andre, S. Duquesne, A. Marty, *Nature*, **2020**, 580, 7802, 216.
- [5] E. Z. L. Zhong-Johnson, C. A. Voigt, A. J. Sinskey, *Sci. Rep.*, **2021**, 11, 1, 928.



# New *N*-aroyl acylhydrazones as tunable photoswitches

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Molecular photoswitches have attracted much interest in several fields, such as photography, protection from sunlight, imaging, solar energy conversion, and storage as well as drug delivery.<sup>[1]</sup> Such molecules are able to reversibly convert from a stable isomer to the thermodynamically less stable one by photoirradiation. This process can be monitored through different spectral behavior of the isomers.<sup>[2]</sup> Examples of belonging to this class are compounds which undergo reversible *E/Z* isomerization or cycloaddition.<sup>[3]</sup> The versatile acylhydrazone RCO–NH–N=CHR' functional group found applications in various fields such as sensing and cation coordination and more recently, in the development of photoswitches.<sup>[4]</sup>

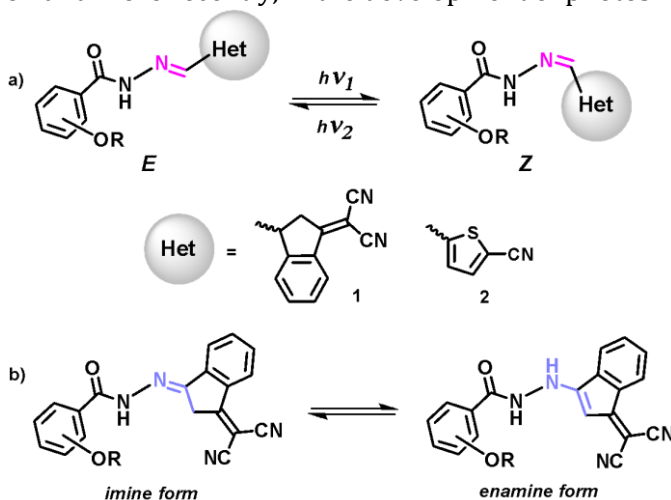


Fig. 1: a) *E/Z* photoisomerization of *N*-aroylhydrazones; b) Imine-enamine tautomerization of derivatives **1**

*N*-aroylhydrazones are promising candidates due to their bistability<sup>[5]</sup>, facile synthesis, high thermal stability, and emission toggling and therefore can be used in development of molecular machines, high-resolution imaging dyes or photoresponsive drugs.<sup>[1,2]</sup>

This work focuses on synthesis, structural characterization, and investigation of the optical and electronic properties of a series of *N*-aroylhydrazones bearing hydroxy/methoxybenzene units and aromatic/heteroaromatic substituents as dicyanoindene or cyanotienyl (Fig. 1). Next, we will look into their switching behavior upon light irradiation based on the *Z/E* isomerization process (Fig. 1a). The preliminary studies on their absorption and emission properties showed substantial changes when alternating the position and the nature of the benzene ring substituent, as for example a notable increase in the emission brightness by replacing the hydroxy group with methoxy. In the case of acylhydrazones bearing dicyanoindene unit, formation of the enamine tautomer was also observed (Fig. 1b). Furthermore, the UV-Vis and fluorescence measurements in different solvents showed strong influence of the polarity of the solvent, the solvatochromism phenomenon being noticed.

- [1] Z. L. Pianowski, B. Shao, I. Aprahamian, *Wiley* **2022**, *1*, 114-132.
- [2] P. M. Toro, D. H. Jara, A. H. Klahn, D. Villaman, M. Fuentealba, A. Vega, N. Pizarro, *Photochem. Photobiol.* **2021**, *97*, 61-70.
- [3] A. Georgiev, P. Todorov, D. Dimov, *J. Photochem. Photobiol., A* **2019**, *386*, 112143.
- [4] X. Su, I. Aprahamian, *Chem. Soc. Rev.* **2014**, *43*, 1963.
- [5] B. C. Enache, A. Hanganu, C. Tablet, C. C. Anghel, C. C. Popescu, A. Paun, N. D. Hădade, A. M. Mădălan, M. Matache, *ACS Omega* **2022**, *7*, 39122–39135.

## **Mono- and binuclear complexes with polydentate imino and amino ligands derived from N-(1-naphthyl)ethylenediamine**

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Polydentate imino and amino ligands play a significant role in the design of homo- and heteropolynuclear complexes containing 3d and 4f metal ions. Typically, the synthesis of such complexes involves a stepwise process in which the 3d ion is introduced first, followed by the use of the resulting complex as a ligand towards the 4f ion.<sup>[1]</sup>

In this study, a series of novel polydentate Schiff base ligands were synthesized using N-(1-naphthyl)ethylenediamine and various phenol aldehydes. These imino ligands and the amino derivatives obtained by reduction were employed either alone or in combination with other chelatic ligands to produce mono- and binuclear complexes. X-ray diffraction on single crystal was utilized to structurally characterize the ligands and complexes. The investigation revealed the versatility of these types of imino and amino derivatives functioning as bidentate, tridentate, or tetradentate ligands. Figure 1 shows the sequential synthesis of a heterobinuclear Zn(II)-Tb(III) complex.

Additionally, the optical properties (IR, UV-Vis, luminescence) of the ligands and complexes were analysed in the solid state.

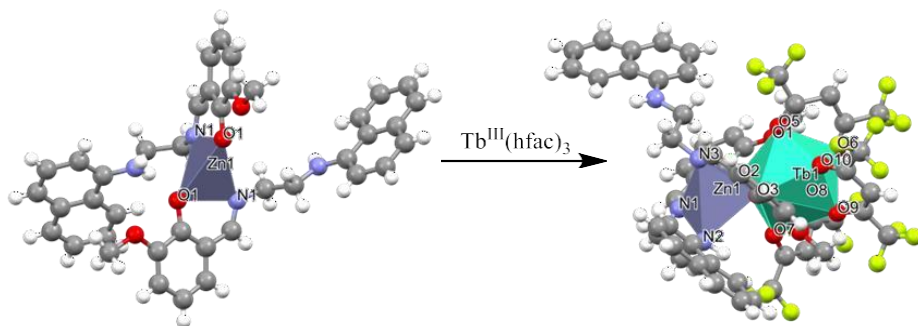


Fig. 1: Stepwise synthesis of a heterobinuclear Zn(II)-Tb(III) complex

[1] M. Sarwar, A.M. Madalan, C. Tiseanu, G. Novitchi, C. Maxim, G. Marinescu, D. Luneau, M. Andruh, *New J. Chem.* **2013**, 37, 2280.

# Gas-phase kinetic studies on the OH radical initiated oxidation of 2- and 4-nitrotoluene

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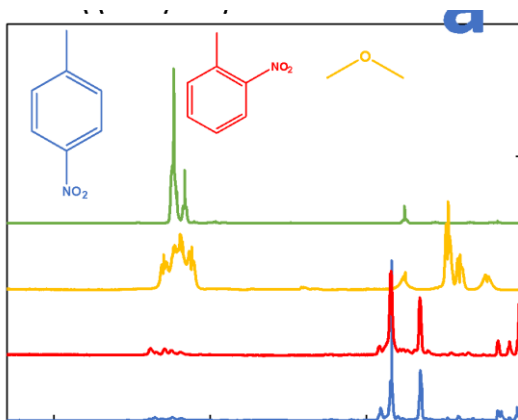


Fig. 1: Gas-phase IR spectra of 2- and 4-nitrotoluene (a and b) and the reference compounds, dimethyl ether (c), and cyclohexane (d)

Nitroaromatic hydrocarbons (NAHs) are ubiquitous compounds in the urban atmosphere, formed as secondary products in the oxidation of primary emitted aromatic compounds. Most of these compounds have toxic, carcinogenic, and mutagenic properties and can affect air quality and human health.<sup>[1]</sup> Direct photolysis of 2-nitrotoluene is thought to produce HONO, which is an important source of OH radical in the urban atmosphere, through a mechanism similar to that proposed by Bejan *et al.* (2006) for 2-nitrophenol.<sup>[2]</sup> Secondary organic aerosols (SOAs) formation is highly expected from nitrotoluenes since other nitroaromatics were found as

SOAs precursors through a photolysis mechanism.<sup>[3]</sup> To our knowledge, there is only one reported rate coefficient in the literature for the oxidation of 3-nitrotoluene with the OH radical:  $k_{3\text{NT}+\text{OH}}=1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>[4]</sup>

The Environmental Simulation Chamber, made of Quartz from University “Alexandru Ioan Cuza” from Iasi (ESC-Q-UAIC) with a volume of 760 L, equipped with long-path FTIR measurement technique, was employed to perform kinetic investigations on the gas-phase reactivity of selected nitrotoluenes towards OH radicals. Investigations were performed at 298 K and 1 atm of synthetic air at a total optical path length of  $(492 \pm 1)$  m. Methyl nitrite and isopropyl nitrite photolysis (at  $\lambda_{\text{max}}=365 \text{ nm}$ ) in the presence of NO was used to generate the OH radicals in the reactor. For the relative rate kinetic method, dimethyl ether (DME) and cyclohexane were used as reference compounds. The kinetic process was monitored over a period of 15-20 minutes with the IR spectra collected each minute at a resolution of  $1 \text{ cm}^{-1}$ . Beforehand, the reactants’ wall loss and photolysis rate were determined to correct the results.

The kinetic rate coefficients for the reaction of 2-nitrotoluene and 4-nitrotoluene with OH radical were obtained in the present study for the first time. The rate coefficients were found to be higher than the rate coefficient for the 3-nitrotoluene isomer. The determined rate coefficients for the gas-phase reaction of selected nitrotoluenes with OH radicals will be compared with the values estimated by the Structure-Activity Relationship kinetic approach. The atmospheric implications would be also assessed and the potential impact on the regional scale discussed.

**Acknowledgement:** Authors acknowledge the financial support offered by PN-III-P2-2.1-PED2021-4119 (SOA-REACTOR) project from UEFISCDI. Acknowledgment is also given to the RECENT AIR project under grant agreement MySMIS no. 127324.

[1] Calvert, J., Atkinson, R., Becker, K.H., Kamens, R., Seinfeld, J., Wallington, T. and Yarwood, G., Oxford University Press, 2002.

[2] Bejan, I.; Abd El Aal, Y.; Barnes, I.; Benter, T.; Bohn, B.; Wiesen, P.; Kleffmann, J., *Phys. Chem. Chem. Phys.* **8** 2028 (2006).

[3] Bejan, I.; Olariu, R.I.; Wiesen, P.; Secondary Organic Aerosol Formation from Nitrophenols Photolysis under Atmospheric Conditions, *Atmosphere*, **11** (12) 1346, (2020).

[4] Atkinson, R., Aschmann, S., Arey, J., Carter, W., *Int. J. Chem. Kinet.*, **21** 801 (1989).

## FALL(s)ing for D-amino acids: a chemo-enzymatic cascade for the production of D-phenylalanine analogues

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D-amino acids, particularly D-phenylalanine analogues, are important chiral building blocks in the pharmaceutical industry, despite their non-proteinogenic nature and their bacterial prevalence.<sup>[1]</sup>

Due to the importance of the stereochemistry in drug synthesis, enzymatic and biocatalytic techniques in the synthesis of these building blocks must be considered. Moreover, these approaches align with the principles of green chemistry and simultaneously improve the selectivity, yield and productivity.

We report here the synthesis of D-phenylalanine analogues using a chemo-enzymatic cascade starting from the corresponding aldehydes **1**. Employing a modified Knoevenagel-Doebner condensation with malonic acid, we generate the *trans*-cinnamic acid derivatives **2**, the first substrate for the one-pot enzymatic component of the cascade. Three primary enzymes are then involved in this process: a rationally designed mutant of phenylalanine ammonia-lyase from *Arabidopsis thaliana* (AtPAL)<sup>[2]</sup> catalyzes the hydroamination of **2** into the L-phenylalanines **3**, which are further oxidized by the L-amino acid deaminase from *Proteus mirabilis* (PmLAAD)<sup>[3]</sup> resulting in the  $\alpha$ -keto acids **4**. Lastly, an engineered D-amino acid dehydrogenase from *Ureibacillus thermosphaericus* (UtDAADH)<sup>[4]</sup> performs the reductive amination of **4** thus, obtaining the d-phenylalanine analogue **5**, while glucose dehydrogenase from *Bacillus subtilis* (BsGDH)<sup>[5]</sup> was employed for cofactor recycling. (Figure 1)

After several optimization steps the cascade was efficiently applied at 0.5 g scale for *meta*- and *para*- substituted D-phenylalanines achieving high yields and ee% values.

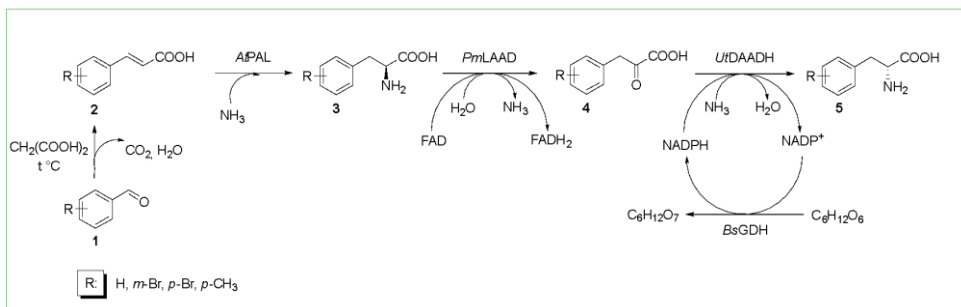


Fig. 1: The chemo-enzymatic synthesis of D-phenylalanine analogues.

- [1] F. Parmeggiani, N.J. Weise, S.T. Ahmed, N.J. Turner, *Chem. Rev. (Washington, DC, U. S.)* **2018**, *118*, 73.
- [2] S.D. Tork, M.E. Moisă, L. Cserepes, A. Filip, L.C. Nagy, F.D. Irimie, L.C. Bencze, *Sci. Rep.* **2022**, *12*, 10606.
- [3] Y. Hou, G.S. Hossain, J. Li, H.D. Shin, L. Liu, G. Du, *Appl. Microbiol. Biotechnol.* **2015**, *99*, 8391.
- [4] H. Akita, J. Hayashi, H. Sakuraba, T. Ohshima, *Front. Microbiol.* **2018**, *9*.
- [5] W.Z. Qian, L. Ou, C.X. Li, J. Pan, J.H. Xu, Q. Chen, G.W. Zheng, *ChemBioChem* **2020**, *21*, 2680.



## Synthesis and structural characterization of novel organobismuth(III) dichloride

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Organobismuth(III) dihalides are a class of organometallic compounds that contain a bismuth atom bonded to two halogen atoms and one organic ligand. Compounds belonging to this class have been studied for their potential use in catalysis, CO<sub>2</sub> fixation and materials science<sup>[1]</sup>.

Overall, the synthesis and study of organobismuth(III) dihalides is an active area of research and new compounds with novel properties are continuously reported in the literature. Recent developments have concluded that efficient steric protection of the metal atom could be provided by aryl groups containing one or two built-in donor ligands (*e.g.* 2-(R<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>, 2-(RN=CH)C<sub>6</sub>H<sub>4</sub>, 2-(ROCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>, 2,6-(R<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-(RN=CR')<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-(ROCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-[(RO)<sub>2</sub>P(O)]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). This protection also reduces Lewis acidity through intramolecular E→Bi (E = N, O) interactions observed both in solution and in solid state<sup>[2]</sup>.

Here we report on the synthesis and structural characterization of [4-*t*Bu-2,6-[(*i*PrO)<sub>2</sub>P(O)]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]BiCl<sub>2</sub> (**2**). The compound was obtained by reacting the lithiated organic ligand (prepared *in situ* from 4-*t*Bu-2,6-[(*i*PrO)<sub>2</sub>P(O)]<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**1**)<sup>[3]</sup> and lithium diethylamide) with freshly sublimed BiCl<sub>3</sub>, using a 1:1 molar ratio, under inert atmosphere of argon (Fig. 1). The enthalpy reaction was estimated using bond energies.

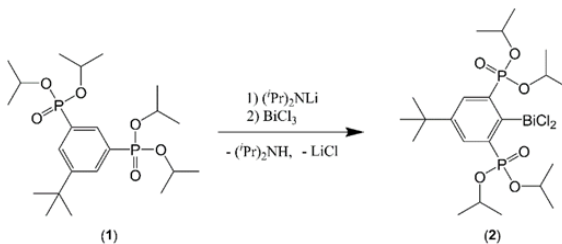


Fig. 1: Synthesis of [4-*t*Bu-2,6- $\{(\text{iPrO})_2\text{P}(\text{O})\}_2\text{C}_6\text{H}_2\text{BiCl}_2$  (**2**).

Compound **2** was characterized by spectroscopic and spectrometric methods - IR, multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $2\text{D}$ ) NMR, MS. The crystal and molecular structure of this organobismuth(III) dichloride was established by single-crystal X-ray diffraction (Fig. 2).

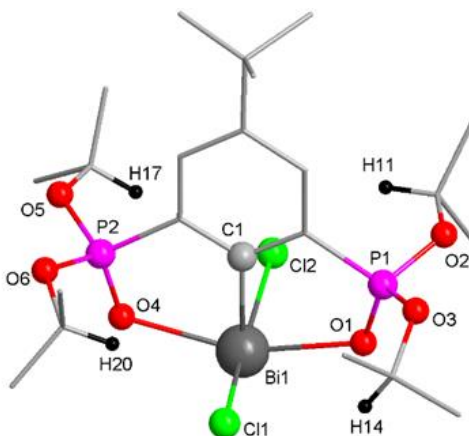


Figure 2. Molecular structure of [4-*t*Bu-2,6- $\{(\text{iPrO})_2\text{P}(\text{O})\}_2\text{C}_6\text{H}_2\text{BiCl}_2$  (**2**).

- [1] (a) C. I. Raț, C. Silvestru, H. J. Breunig, *Coord. Chem. Rev.*, **2013**, 257, 818-879; (b) C. I. Raț, A. Soran, R. A. Varga, C. Silvestru, *Adv. Organomet. Chem.*, **2018**, 70, 233-311; (c) E. Lopez, S. C. Thorp, R. S. Mohan, *Polyhedron*, **2022**, 222, 115765; (d) H. W. Moon, J. Cornella, *ACS Catal.*, **2022**, 12, 1382-1393.
- [2] (a) A. P. Soran, C. Silvestru, H. J. Breunig, G. Balázs, J. C. Green, *Organometallics*, **2007**, 26, 1196-1203; (b) A. Soran, H. J. Breunig, V. Lippolis, M. Arca, C. Silvestru, *Dalton Trans.*, **2009**, 77-84; (c) K. Peveling, M. Schürmann, S. Herres-Pawlis, C. Silvestru, K. Jurkschat, *Organometallics*, **2011**, 30, 5181-5187.
- [3] M. Henn, V. Deáky, S. Krabbe, M. Schürmann, M. H. Prosenc, S. Herres-Pawlis, B. Mahieu, K. Jurkschat, *Z. Anorg. Allg. Chem.*, **2011**, 637, 211-223.

## Getting positive! Increasing the electrostatic potential on antimony using chelating ligands with electron-withdrawing substituents

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$\sigma$ -Hole interactions generally occur between regions of high and low molecular electrostatic potential of different molecules. These weak interactions have recently been used in catalysis to selectively obtain certain reaction products, unavailable by other means.<sup>[1,2]</sup>

We report the molecular structure of the tetrahydrofuran adduct of  $\text{PhSbCl}_2(o\text{-O}_2\text{C}_6\text{Cl}_4)$  (**1**) and the synthesis and characterization of  $[\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}]\text{Sb}[\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{OH}]$  (**2**) (Fig. 1). Spectroscopic characterization of **1** was previously reported in literature.<sup>[3]</sup>

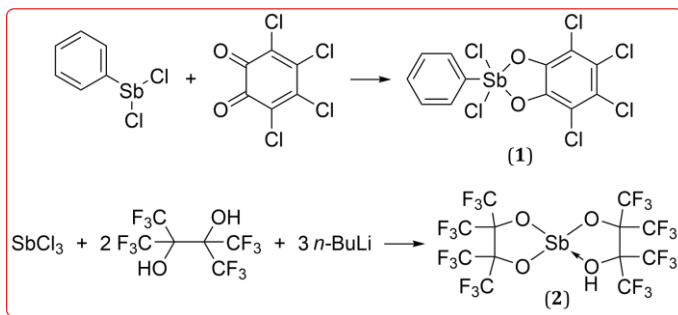


Fig. 1: Syntheses of **1** and **2**.

To gauge the Lewis acidity and  $\sigma$ -hole depth theoretical fluoride ion affinity (FIA)<sup>[4]</sup> and molecular electrostatic potential (MEP) of **1** and **2** (Fig. 2) along with five other compounds that have been previously presented (Fig. 3). To corroborate the theoretical studies with spectroscopic data on Lewis acidity Gutmann-Beckett and Child NMR experiments were performed.

These compounds could be useful catalysts in supramolecular assembly reactions mediated by noncovalent interactions.

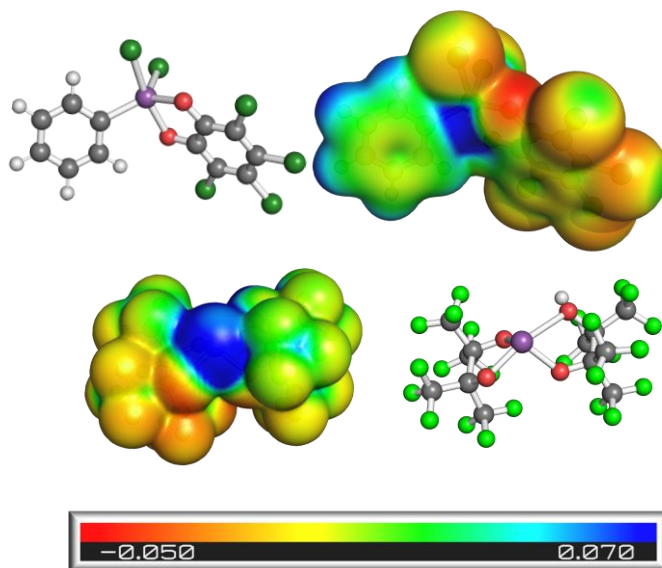


Fig. 2: Projection of the molecular electrostatic potential onto a 0.003 a.u. isodensity surface for the single molecule optimized geometries (PBEh-3c/def2-mSVP level of theory).

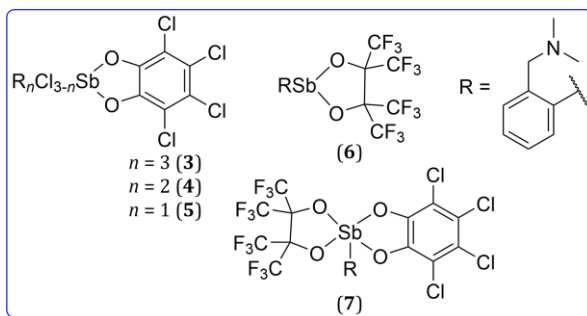


Fig. 3: List of other theoretically characterized compounds in this work.

- [1] A. Gini, M. Paraja, B. Galmés, C. Besnard, A. I. Poblador-Bahamonde, N. Sakai, A. Frontera, S. Matile, *Chem. Sci.* **2020**, *11*, 7086–7091.
- [2] M. Paraja, A. Gini, N. Sakai, S. Matile, *Chem. - Eur. J.* **2020**, *26*, 15471–15476.
- [3] M. N. Gibbons, M. J. Begley, A. J. Blake, D. Bryan Sowerby, *J. Chem. Soc., Dalton Trans.* **1997**, 2419–2426.
- [4] P. Erdmann, J. Leitner, J. Schwarz, L. Greb, *ChemPhysChem* **2020**, *21*, 987–994.

# **Tuning aromaticity by substituent effects. A computational study on inorganic benzene-like compounds**

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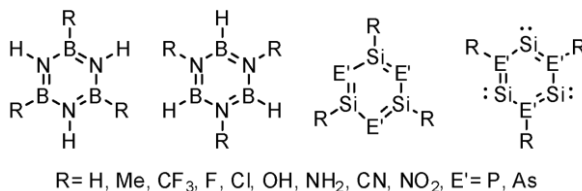
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The enhanced (in)stability and specific reactivity of  $\pi$ -delocalized planar organic cyclic systems is usually related to a chemical property named (anti)aromaticity. Although being a central concept in organic chemistry, aromaticity also occurs in inorganic compounds such as borazine, *i.e.* the first synthesized inorganic “aromatic” ring. Subsequently, many other inorganic benzene-like cycles were synthesized and fully characterized, especially by Power and others.<sup>[1,2,3]</sup> Even though these compounds are presumably aromatic, most of them have only been obtained in special conditions, while bulky substituents are usually used to achieve their kinetic stabilization.

Among the most popular experimental methods for assessing the aromaticity of organic compounds, include the evaluation of the hydrogenation reaction enthalpies or the specific chemical shifts in  $^1\text{H}$ -NMR, which are widely employed. Regarding inorganic aromatic rings, there is no universal experimental method developed so far. Yet, structural criteria such as the planarity of the cycle or the equality of the bond lengths are the only aromaticity indicators for these species. However, up to date, the most used methods in evaluating the aromaticity of inorganic compounds are based on molecular modelling. These include the calculations of specific indices based on different types of aromatic criteria: geometric (HOMA), energetic (ASE), electronic (PDI, FLU,  $I_{\text{ring}}$ ), and magnetic (NICS, ACID).

The current study aims to investigate the impact of substituent effects on several inorganic benzene-like systems, such as  $\text{B}_3\text{H}_6\text{N}_3$ ,  $\text{Si}_3\text{H}_3\text{P}_3$ ,  $\text{Si}_3\text{P}_3\text{H}_3$ ,  $\text{Si}_3\text{H}_3\text{As}_3$  and  $\text{Si}_3\text{As}_3\text{H}_3$  (Scheme 1), in order to see the fluctuations in the aromatic indices. The correlation between them has been evaluated to understand if different aromatic criteria vary in the same way (as in Figure

1). All these calculations are carried out at the DFT level of theory, in conjunction with the following methods: Natural Bond Orbital theory (NBO), Bader's Quantum Theory of Atoms in Molecules (QTAIM) and Nucleus Independent Chemical Shift (NICS).<sup>[4,5,6]</sup>



Scheme 1. Cyclic B<sub>3</sub>R<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, B<sub>3</sub>H<sub>3</sub>N<sub>3</sub>R<sub>3</sub>, Si<sub>3</sub>R<sub>3</sub>E'<sub>3</sub>, and Si<sub>3</sub>E'<sub>3</sub>R<sub>3</sub> models investigated in the current study

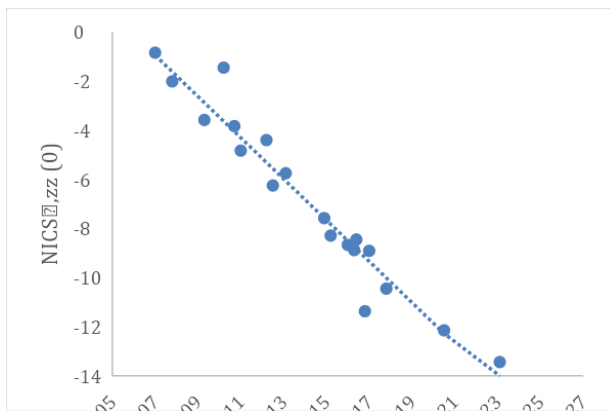


Figure 1. The graphical representation of  $\text{NICS}_{\pi, \text{zz}}(0) = f(\text{PDI})$  for B<sub>3</sub>R<sub>3</sub>N<sub>3</sub>H<sub>3</sub> and B<sub>3</sub>H<sub>3</sub>N<sub>3</sub>R<sub>3</sub> systems

- [1] P. P. Power, *J. Organomet. Chem.* **1990**, 400, 49–69.
- [2] K. M. Waggoner, H. Hope, P. P. Power, *Angew. Chemie Int. Ed. English* **1988**, 27, 1699–1700.
- [3] A. E. Seitz, M. Eckhardt, A. Erlebach, E. V. Peresyphkina, M. Sierka, M. Scheer, *J. Am. Chem. Soc.* **2016**, 138, 10433–10436.
- [4] E. D. Glendening, C. R. Landis, F. Weinhold, *WIREs Comput. Mol. Sci.* **2012**, 2, 1–42.
- [5] J. Cioslowski, E. Matito, M. Solà, *J. Phys. Chem. A* **2007**, 111, 6521–6525.
- [6] A. Stanger, *J. Phys. Chem. A* **2019**, 123, 3922–3927.

# Effect of Phosphorus and Nitrogen Heteroatoms on Pentahapto Coordination of Diazaphosphole Ligands in Binuclear Iron Carbonyl Derivatives

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The landmark discovery in 1951 of ferrocene exhibiting a novel sandwich structure having an iron atom sandwiched between two planar cyclopentadienyl rings has been followed by development of extensive chemistry of cyclopentadienyl metal carbonyls. The chemistry of the cyclopentadienyliron carbonyl system is particularly rich. Thus decarbonylation<sup>[1,2]</sup> of the binuclear derivative  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  leads to several interesting products including the interesting stable triplet spin state derivative  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$  (Figure 1).

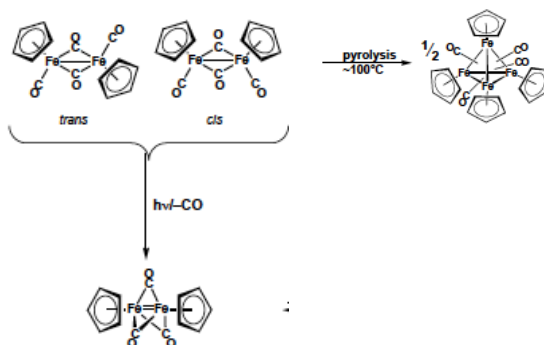


Figure 1. Some cyclopentadienyliron carbonyl derivatives.

The chemistry of cyclopentadienyl metal complexes is characterized by pentahapto bonding of the  $\text{C}_5$  ring to a central metal atom. Of interest is the preservation of the pentahapto mode of bonding when a CH vertex of the pentagonal ring is replaced by an isoelectronic bare nitrogen or

phosphorus atom. Complete preservation of pentahapto bonding has been shown for complete substitution of all five CH groups in the cyclopentadienyl ligand with phosphorus atoms in the pentaphosphaferrocene derivative ( $\eta^5\text{-Me}_5\text{C}_5$ )Fe( $\eta^5\text{-P}_5$ ). We have now used density functional theory to determine the preferred bonding modes of the diazaphospholyl ligand in the binuclear  $(\text{Me}_2\text{C}_2\text{N}_2\text{P})_2\text{Fe}_2(\text{CO})_n$  ( $n = 4, 3, 2, 1$ ) systems in order to ascertain the effect of the two nitrogen heteroatoms.

Our results from these studies were rather disappointing since a complicated energy surface with a large number of energetically closely spaced structures were found for each of these systems. However, an important conclusion from this work is that higher spin state quintet and triplet structures with partially bonded rather than singlet pentahapto bonded diazaphospholyl rings were clearly energetically preferred in these systems. The lowest energy structures for  $(\text{Me}_2\text{C}_2\text{N}_2\text{P})_2\text{Fe}_2(\text{CO})_4$  and  $(\text{Me}_2\text{C}_2\text{N}_2\text{P})_2\text{Fe}_2(\text{CO})_3$  are shown in Figure 2 as examples of such structures. However, each of these structures, which exhibit quintet spin states, lies less than 2 kcal/mol below the next of a number of energetically closely spaced isomers suggesting that in these systems density functional methods are not able to define a uniquely favorable structure. We are in the process of extending these studies to the analogous ruthenium systems  $(\text{Me}_2\text{C}_2\text{N}_2\text{P})_2\text{Ru}_2(\text{CO})_n$  ( $n = 4, 3, 2, 1$ ). We hope that the larger ligand field splittings in ruthenium complexes relative to analogous iron complexes will lead to simpler potential energy surfaces thereby clearly indicating the preferred modes of bonding of the diazaphospholyl ligands in binuclear metal carbonyl derivatives of various types.

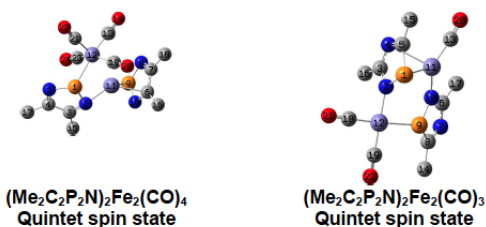


Figure 2. The lowest energy  $(\text{Me}_2\text{C}_2\text{P}_2\text{N})_2\text{Fe}_2(\text{CO})_n$  ( $n = 4, 3$ ) structures.

[1] J. P. Blaha, B. E. Bursten, J. C. Dewan, R. B. Frankel, C. L. Randolph, B. A. Wilson, M. S. Wrighton, *J. Am. Chem. Soc.*, **1985**, *107*, 4561.

[2] X. Chen, L. Yuan, G. Ren, Q. Xi, R. Jin, Q. Dua, H. Feng, Y. Xie, R. B. King, *Inorg. Chim. Acta*, **2016**, *445*, 79



## **Preliminary study of the influence of sweeteners on the bioavailability of polyphenols in lingonberry jams**

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The object of this work is to investigate the influence of some sweeteners on the bioavailability of polyphenolic compounds in lingonberry jams.

Dietary habits have changed as people are more and more interested in eating natural products. Lingonberries are fruits known for their high content of polyphenolic compounds, vitamins, anthocyanins, minerals and polysaccharides.<sup>[1]</sup> At the same time, lingonberries are known for their beneficial effects on the urinary tract, the immune system and are known for their anti-diabetic effect.<sup>[2]</sup>

In order to evaluate the beneficial effects of bioactive compounds on the human body, an analysis is required that takes into account the changes that may occur during gastro-intestinal digestion. Simulation of gastro-intestinal digestion is used as an in vitro method to study compounds in plants, foods and pharmaceuticals.<sup>[3]</sup>

To evaluate the bioavailability of polyphenolic compounds, healthy cells and colon cancer (Caco-2) cells were grown for 26 days, changing medium every 3 days. The transepithelial electrical resistance (TEER) of cells grown in Transwell medium was measured using Millicell ERS-2 Voltohmmeter 1 and only monolayers with resistance greater than 400  $\Omega\text{cm}^2$  are used for experiments.

Following gastro-intestinal digestion, jams were inserted into cells and sampled after 0, 30, 60, 90, 120 minutes and stored in the freezer until analysis. In this way, the analysis of polyphenolic compounds in these samples indicates the amount of polyphenols absorbed into the blood.<sup>[4]</sup>

The total polyphenol content was determined by the spectrophotometric Folin-Ciocalteu method<sup>[5]</sup> and the individual polyphenol content by chromatographic analysis.

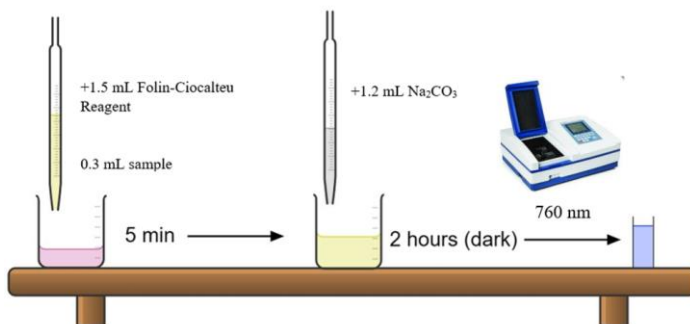


Fig. 1: Folin-Ciocalteu method

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- [1] P. Kylli, L. Nohynek, R. Puupponen-Pimia, B. Westerlund-Wikstrom, T. Leppanen, J. Welling, E. Moilanen, M. Heinonen, *J. Agric. Food Chem.* **2011**, 59, 3373.
- [2] K. A. Ross, Y. Siow, S. C. Debnath, *Chapter 27 – Lingonberries in Nutritional Composition and Antioxidant Properties of Fruits and Vegetables*, Academic Press, Dublin, **2020**.
- [3] M. Minekus, M. Almingier, P. Alvito, S. Ballance, T. Bohn, C. Bourlieu, F. Carrière, R. Boutrou, M. Corredig, D. Dupont, *Food Funct.* **2014**, 5, 1113.
- [4] A. Cilla, A. González-Sarrías, F. A. Tomás-Barberán, J. C. Espín, R. Barberá, *Food Chem.* **2009**, 114, 813.
- [5] V.L. Singleton, R. Orthofer, R.M. Lamuela-Raventos, *Meth. Enzymol.* **1999**, 299, 152.

## Solid-Phase Synthesis of an Epoxysuccinyl Functionalized Peptide as Potential Activity-Based Probe for Cathepsin B

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Activity based probes (ABPs) are powerful chemical tools for investigation of biological processes, such as proteomic studies.<sup>[1,2]</sup> ABPs act by irreversibly modifying the active site of an enzyme, in a manner that can be directly correlated with its activity. ABPs possess three main structural components (Fig.1, top): a reactive group (also known as „warhead”) for reaction with the target enzyme, usually represented by known mechanism-based inhibitors of the target, an affinity region (i.e. a short peptide sequence) required to direct reactivity to the active site, a linker that is most often a hydrophobic/ hydrophilic chain required to modulate solubility and avoid steric hindrance and an analytical handle (detection tag), such as biotin, for the visualization and purification of the modified enzyme.<sup>[1]</sup>

In this context we focused on developing a new ABP that has an epoxysuccinate-based “warhead” (Fig. 1, bottom). The epoxide is a common inhibitor for the papain family, which irreversibly forms a thioether bond with the active site cysteine. This reactive group was observed in nature under the form of epoxysuccinates, part of the product E-64 (*L-trans*-epoxysuccinyl-leucylamido(4-guanidino)butane).<sup>[2]</sup>

To get access to the target ABP we first functionalized L-lysine and biotin with azide, and alkyne groups, respectively, as reactive groups required to perform the copper (I) catalyzed alkyne-azide cycloaddition (CuAAC) *click* reaction, for the connection of the detection tag to the linker. CuAAC is well known to show high yields, high bioorthogonality, and to take place under mild reaction conditions. The linker, peptide sequence and warhead were assembled by solid phase peptide synthesis (SPPS) method, Fmoc chemistry.<sup>[3]</sup>

The azide and alkyne modified compounds were characterized by NMR spectroscopy and mass spectrometry, while the ABP was analysed by RP-HPLC-MS.

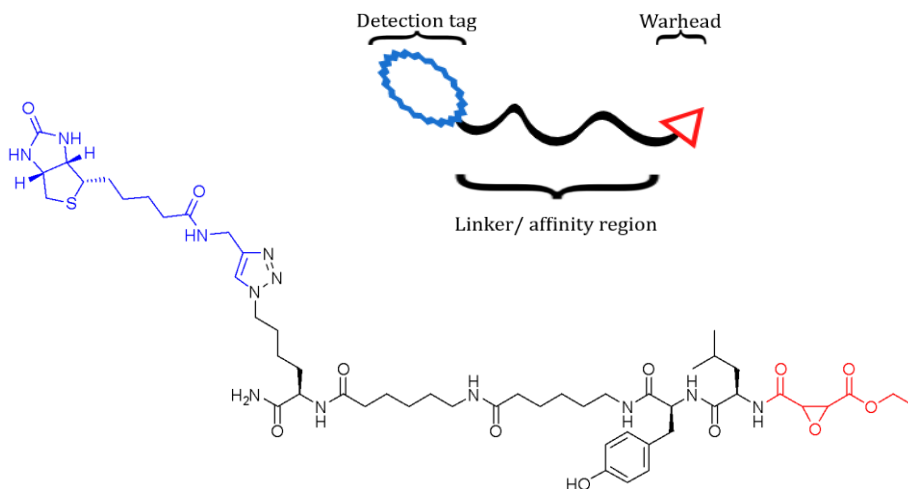


Fig. 1: Main components of an ABP (top)  
Structure of target ABP (bottom)

Our future work will be directed toward the use of this ABP in order to assess Cathepsin B activity, a member of the papain family.

- [1] H. Fang, B. Peng, S. Y. Ong, Q. Wu, L. Li, S. Q. Yao, *Chem. Sc.* **2021**, *12*, 8288–8310
- [2] M. J. Evans, B. F. Cravatt, *Chem. Rev.* **2006**, *106*, 3279–3301
- [3] D. M. M. Jaradat, *Amino Acids* **2018**, *50*, 39–68

## Synthesis of alkyl enol ethers

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Olefins are among the most important and widely used building blocks in organic synthesis. An interesting subgroup of olefins is the alkoxy substituted olefins, the so-called alkyl enol ethers. This structural moiety is present in a wide range of natural products and biologically active molecules, as well as intermediates in the pharmaceutical industry.<sup>[1,2]</sup> Due to conjugation effect, the alkoxy substituent greatly enhances the regioselectivity of the reactions and strongly polarizes these molecules, thus creating additional opportunities for their utilization as building blocks. Accordingly, they are valuable reagents for a large number of transformations, including Heck and related cross-coupling reactions, cycloaddition reactions, [3,3]-sigmatropic rearrangements or metathesis reactions.<sup>[3]</sup>

Numerous methods are known for the synthesis of alkyl enol ethers, but these often suffer from various difficulties, hampering the exploration of these molecules. Indeed, classical preparations of alkyl enol ethers require harsh conditions as well as expensive reagents or have a very narrow substrate scope.<sup>[4]</sup> Herein we present a new method for the synthesis of alkyl enol ethers which utilizes the catalytic hydrosilylation of esters.

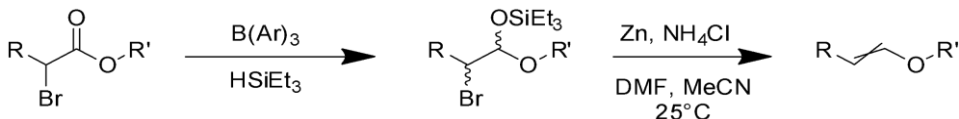


Fig. 1: Synthesis of alkyl enol ethers.

The use of non-metallic, frustrated Lewis pair (FLP) based catalysts could overcome some of these problems, as presented in the work of Soós et al.<sup>[5]</sup> The subsequent elimination reaction uses safe and cheap reagents, as well as undergoes smoothly under mild conditions.

- [1] Poulsen, T. B. Total synthesis of natural products containing enamine or enol ether derivatives. *Acc. Chem. Res.* **2021**, *54* (8), 1830-1842.
- [2] Yousefi, R.; Paul-Gorsline, B. J.; Soltani, O.; Ashtekar, K. D. An Alternative Route to the Anticancer Agent: 2-Fluorofucose from Readily Available L-(-)Rhamnose and Mechanistic Insights into a Zinc/Ammonium Iodide-Mediated Elimination Reaction. *Org. Process Res. Dev.* **2022**, *26* (8), 2475-2482.
- [3] Ahmad, S. A. Z.; Jena, T. K.; Khan, F. A. Alkyl enol ethers: Development in intermolecular organic transformation. *Chem. Asian J.* **2021**, *16* (13), 1685-1702.
- [4] Evano, G.; Gaumont, A.-C.; Alayrac, C.; Wrona, I. E.; Giguere, J. R.; Delacroix, O.; Bayle, A.; Jouvin, K.; Theunissen, C.; Gatignol, J. Metal-catalyzed synthesis of hetero-substituted alkenes and alkynes. *Tetrahedron* **2014**, *8* (70), 1529-1616.
- [5] T. Soós, Á. Gyömöre, Á. Dudás, D. Fegyverneki, M. Gyöngyösi, P. Sőregi, N. Kolozsvári, Triaryl borane catalysts and method for selective hydrosilylation of esters and lactones using said catalysts. WIPO Patent Application WO/2022/129966, June 23, 2022

## Synthesis and structural characterization of diarylbismuth(III) nicotines and isonicotines

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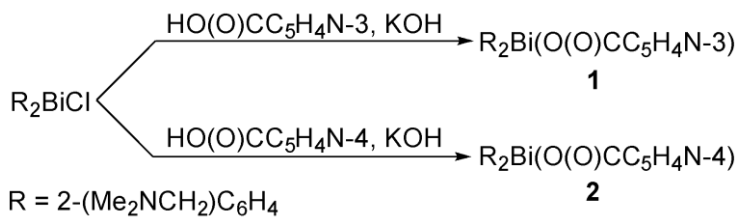
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Heterometallic coordination compounds are a relatively new and interesting field in inorganic chemistry. The use of heavy pnictogens in such compounds is still underdeveloped. Nevertheless, the unique properties of antimony and especially of bismuth opens new pathways in the chemistry of heterometallic compounds containing these elements.

In heterometallic complexes, one of the metal atoms is often part of a ligand, also known as *metalloligand*, which coordinates to the other metal center. A common approach for the synthesis of complexes is to synthesize first the metalloligand, and then to coordinate it to a different metal atom or ion.<sup>[1]</sup> Following this approach, previous work in our group succeeded the synthesis of bismuth(V)-based heterometallic coordination polymers, using triarylbismuth(V) dicarboxylates as spacers between silver(I) ions. The carboxylate ligands used were nicotinate and isonicotinate and they are coordinated to bismuth center through one oxygen atom and to the silver center through the nitrogen atom of the aromatic heterocycle.<sup>[2]</sup>

We report the synthesis and spectroscopic characterization of diorganobismuth(III) carboxylates  $R_2BiL$  [ $R = 2-(Me_2NCH_2)C_6H_4$ ;  $L = O(O)CC_5H_4N-3$  (**1**),  $O(O)CC_5H_4N-4$  (**2**)]. Compounds **1** and **2** were prepared starting from the diarylbismuth(III) chloride  $R_2BiCl$  and the corresponding acid in the presence of potassium hydroxide (Scheme 1). Compounds **1** and **2** were characterized by  $^1H$ ,  $^{13}C$  NMR and IR spectroscopy and mass spectrometry. The chemical bonding in **1** and **2** was investigated by DFT methods



Scheme 1. Synthesis of **1** and **2**.

[1] S. Srivastava, R. Gupta, *CrystEngComm* **2016**, *18*, 9185.

[2] A. Ben Kiran, T. Mocanu, A. Pöllnitz, S. Shova, M. Andruh, C. Silvestru, *Dalton Trans.* **2018**, *47*, 2531.



## Monitoring and control of rheological proprieties of impression materials

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Although digitalization techniques make progress in dentistry for capturing teeth and jaw data, traditional impressions continue to be a crucial element in everyday dental practices.<sup>[1]</sup> Impression is the negative likeness or copy in reverse of the surface of an object (GPT :Glossary of prosthodontic term 9). It is made by placing an appropriate material in a stock or custom dental impression tray which is designed to roughly fit over the dental arches.<sup>[2]</sup> New elastomeric impression materials, such as polysiloxane, have been introduced in the last decades, promising exceptional elastic recovery and impressive tear and tensile strength.<sup>[3]</sup> The increasing adoption and interest in dental polymers can be attributed not only to their attractive surfaces, but also their favorable mechanical and biological properties, affordability, and ease of handling for a wide range of applications.<sup>[4]</sup>

Achieving an accurate impression, along with flexible recovery and mechanical strength, is heavily dependent on the flow properties.<sup>[4]</sup> Given the potential presence of saliva and blood during the standard impression-making process, the material hydrophobicity may negatively affect the accuracy of the resulting cast.<sup>[5]</sup> Additionally, for the patient's comfort, setting time is a crucial characteristic as it can be an uncomfortable process, particularly for individuals with a sensitive gag reflex. Sadly, there is inadequate information available regarding the present state of elastomers for dental impressions. Most of the literature is outdated and refers to material properties from the late 1990s and early 2000s.<sup>[1]</sup>

This work focuses on presenting the results on rheological proprieties of two commercially available polysiloxane impression materials that were

subjected to oscillatory tests with an Anton Paar rheometer (Model Physica MCR 501; Austria, Graz). A 50-mm diameter stainless steel parallel plate assembly with a 0.5 mm gap was used. Hydrophilicity was evaluated by water contact angle measurement for each material before and during setting. For contact angle determination, drop analysis program plugged in EASYDROP Shape Analysis System (KRÜSS) was used.

In conclusion, our study reflects HOW rheological and goniometric experiments can provide valuable insights into the polysiloxane impression material behavior before and after setting and consequently the ease in handling and the accuracy of the imprint. This discussion confines itself to rheological proprieties and hydrophilicity, but other characteristics such as tear resistance or tensile properties may be determined and correlated with present results.

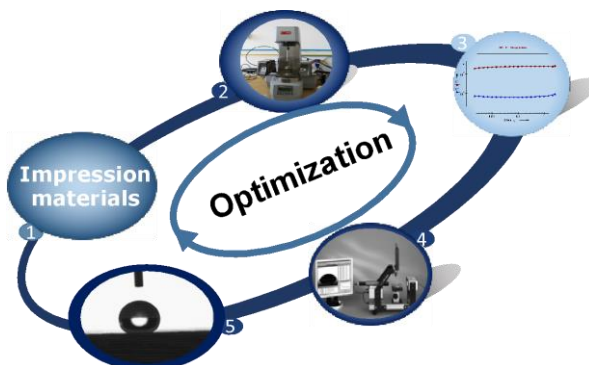


Fig. 1: Impression material recipe optimization process

- [1] F. Huettig, A. Klink, A. Kohler, M. Mutschler, F. Rupp, *Materials*, **2021**, 14, 2994.
- [2] S. Pisulka, S. Nimonkar, A. Borle, Y. Dhage, *EAS J Dent Oral Med*, **2019**, 1, 83.
- [3] D. Re, F. De Angelis, G. Augusti, D. Augusti, S. Caputi, M. D'Amario, C. D'Arcangelo, *Int. J. Dent.*, **2015**, 428286
- [4] R. Samantaray, A. Mohapatra, S. S. Das, K. Nanda, S. Bharadwaj, *Indian J. Forensic Med. Toxicol.*, **2020**, 14, 8884.
- [5] A. Theocharidou, K. Tzimas, K. Tolidis, D. Tortopidis, *Acta stomatol Croat.*, **2021**, 55, 256

# *POSTERS*



## **Novel Aromatic Ammonia Lyases: uncut diamonds with enhanced activity towards challenging L-phenylalanine analogues**

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Unnatural phenylalanine derivatives, especially those with electron donating aromatic substituents are highly valuable chiral building blocks used in the agrochemical and the pharmaceutical industries. Among these derivatives 3,4-dimethoxy-L-phenylalanine is prominent as an intermediate in the synthesis of the anti-Parkinson drug L-DOPA.<sup>[1]</sup>

Phenylalanine ammonia-lyases (PALs) have emerged as a powerful tool to produce optically pure L-phenylalanines, providing a greener approach with high conversion rates and maximised atom economy. One of the main drawbacks of this enzyme family is their low affinity towards electron donating polysubstituted substrates, a problem which so far could not be solved by the means of protein engineering.<sup>[2]</sup>

Recently, using data mining tools we found a novel aromatic ammonia- lyase from *Loktanella atrilutea* (LaAAL) with catalytic residues distinct from phenylalanine/histidine/tyrosine ammonia-lyases (PAL/HAL/TAL). LaAAL is closely related to AL-11, a newly discovered ammonia-lyase with unusually high activity towards electron donating substrates, including 3,4-dimethoxy- L-phenylalanine (Fig. 1).<sup>[3]</sup> In this study, we focused on the exploration of its substrate domain and catalytic activity.

The unique catalytic signature of these two novel enzymes suggests they belong to a different PAL subclass<sup>[4]</sup>, thus we searched for LaAAL/AL-11 homologues using BLAST (Basic Local Alignment Search Tool) and selected those AALs with the highest rates of coverage and

identity values above 60%. Through a phylogenetic tree analysis of these homologues together with known PALs/HALs/TALs we intended to demonstrate the evolutionary relationships between these enzymes. In addition, based on the comparison of the catalytic sites of the homologues, different residues were identified in the hydrophobic pocket. Matching point mutations were introduced to *LaAAL* to assess whether these residues provide further improvements to *LaAAL* towards di- and tri-substituted substrates including lignin derived monomers. Their conversion-based activities were finally determined and compared within the ammonia addition and elimination reaction.

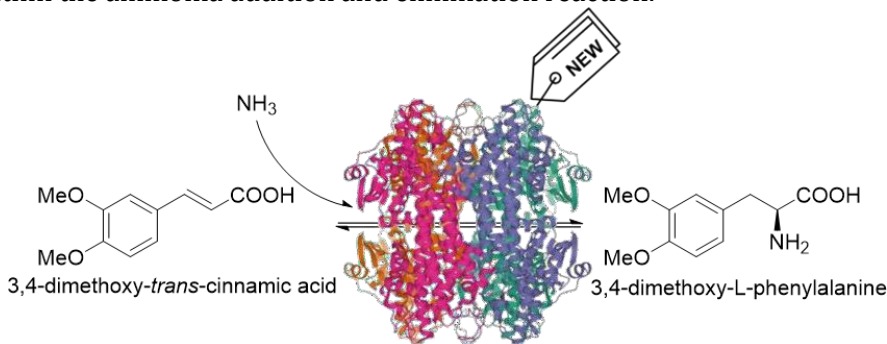


Fig. 1: Ammonia addition reaction of 3,4-dimethoxy-*trans*-cinnamic acid catalyzed by  
*LaAAL*

- [1] F. Parmeggiani, S. T. Ahmed, N. J. Weise, N. J. Turner, *Tetrahedron*, **2016**, 72, 46, 7256-7262
- [2] S. D. Tork, M. E. Moisa, L. Cserepes, A. Filip, L. C. Nagy, F. D. Irimie, L. C. Bencze, *Sci Rep*, **2022**, 12, 1, 10606
- [3] E. E. Kempa, J. L. Galman, F. Parmeggiani, J. R. Marshall, J. Malassis, C. Q. Fontenelle, J. B. Vendeville, B. Linclau, S. J. Charnock, S. L. Flitsch, N. J. Turner, P. E. Barran, *JACS Au*, **2021**, 1, 4, 508-516
- [4] R. B. Tomoiaga, S. D. Tork, A. Filip, L. C. Nagy, L. C. Bencze, *Appl Microbiol Biotechnol*, **2023**, 107, 4, 1243-1256

## **TiO<sub>2</sub> in biopolymer – based composites for skin protection**

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The skin serves as a barrier between the body's internal organs and the outside world. Every day, the skin can be impacted by internal or external factors, and without adequate protection, the skin ages and becomes unhealthy.<sup>[1]</sup>

Tissue engineering is an interdisciplinary field that aims to promote the quality of human life by repairing, preserving, or enhancing the function of tissues and organs previously harmed by trauma, pollution, or radiation.<sup>[2]</sup> Naturally derived polysaccharides such as alginate (Alg) and chitosan (CS) are widely used as biomaterials for tissue treatment applications because, through chemical and physical modifications, their biocompatibility, non- toxicity, and biodegradability properties can be improved. CS accelerates wound healing by stimulating the fibroblasts, macrophages, and inflammatory cells.<sup>[3]</sup> Additionally, Alg is biocompatible, anti-inflammatory, and has good scaffold - forming proprieties.<sup>[4]</sup> On the other hand, researchers have gained interest in titanium dioxide (TiO<sub>2</sub>) because of its good stability under UV radiation, good catalytic activity, and opacity.

Thus, the aim of this study is to obtain hybrid composites made of Alg and CS biopolymers and TiO<sub>2</sub> and to analyze the effect of TiO<sub>2</sub> on the structure of the samples exposed to solar irradiation. First, the as prepared samples were investigated by X-ray diffraction and FT-IR spectroscopy to find insights into their structure. Then the composites

were immersed in simulated body fluid (SBF) and exposed to solar simulator radiation. Finally, the structure of these samples was also examined by FT-IR spectroscopy and X-ray diffraction and the role of  $\text{TiO}_2$  under solar radiation was evidenced. These results can be further used to design new composites to protect the skin from sun's rays.

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- [1] kin UV Protection: A Review," *Photochem Photobiol*, **2020**, 96(4), 779–797, doi: 10.1111/php.13208.
- [2] S. Caddeo, M. Boffito, and S. Sartori, "Tissue Engineering Approaches in the Design of Healthy and Pathological In Vitro Tissue Models," *Front Bioeng Biotechnol*, **2017**, 5, doi: 10.3389/fbioe.2017.00040.
- [3] Matica, Achmann, Tøndervik, Sletta, and Ostafe, "Chitosan as a Wound Dressing Starting Material: Antimicrobial Properties and Mode of Action," *Int J Mol Sci*, **2019**, 20(23), 5889, doi: 10.3390/ijms20235889.
- [4] T. G. Sahana and P. D. Rekha, "Biopolymers: Applications in wound healing and skin tissue engineering," *Mol Biol Rep*, **2018**, 45(6), 2857–2867, doi: 10.1007/s11033-018-4296-3.



# Chlorite dismutase: computational study of the mechanism

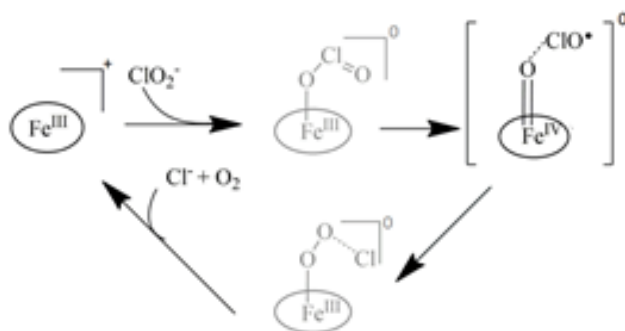
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Chlorite dismutase (Cld) is one of the very few enzymes that can form oxygen-oxygen bonds.<sup>[1]</sup> Cld has been reported in a narrow class of anaerobic bacteria<sup>[2]</sup> that are able to use perchlorate as final electron acceptor for their electron transport chain / respiration.<sup>[3]</sup> The catalytic cycle of Cld has been proposed to involve chlorite binding to the active site heme, followed by cleavage of one of the Cl–O bonds with formation of a formally high-valent iron-oxo center alongside a ClO molecule/ion, and then reattachment of the ClO to the iron-bound oxo atom, followed by liberation of chloride and of molecular oxygen (cf. Scheme 1). However, direct experimental confirmation for the existence of a chlorite-heme adduct in Cld is still unavailable – nor is it clear what the coordination mode of the chlorite is. Moreover, the subsequent reaction intermediates have not been observed directly in experiments. Reported here are density functional theory (DFT) results on the catalytic cycle of chlorite dismutase.



Scheme 1. The catalytic cycle of chlorite dismutase. Shown in grey are the intermediates, which, according to our DFT data, are proposed to be undetectable

Regarding the first intermediate of the catalytic cycle (ferric heme bound to chlorite), the relative energies of the possible linkage isomers and spin states suggest that the binding of the ligand is much more feasible via the oxygen atom (as indeed depicted in Scheme 1). Importantly, this binding leads, with a negligible energy barrier, to a homolytic cleavage of the  $\text{ClO}_2^-$  ligand, resulting in two neutral radicals, namely the formation of a  $\text{Fe(IV)=O}$  species and a hypochlorite radical. The fact that the ligand converts so easily during the geometry optimization at the DFT level indicates a very important thing - namely that it is very unlikely that a ferric-chlorite adduct can be observed experimentally - or, if it is observable, extreme conditions will be needed to stabilize it (either extremely low temperatures, or a sterically constrained environment, or both).

For the third intermediate, the DFT results also suggest no well-defined local energetic minimum, as it decomposes with an extremely small barrier. The chlorine atom is 2.03 Å from the oxygen atom, a very elongated bond that suggests that it can only exist in the form of a complex with the captive chloride ion, alongside an  $\text{Fe(III)}$  heme and an essentially neutral  $\text{O}_2$  moiety.

Consequently, according to our DFT data, the only Cld catalytic cycle intermediate that could be isolated experimentally is the second intermediate,  $\text{Fe(IV)=O}$  heme with a  $\text{ClO}$  radical in the vicinity, possibly magnetically coupled with each other.

[1] A. Q. Lee, B. R. Streit, M. J. Zdilla, M. M. Abu-Omar, J. L. DuBois, *Proc. Natl. Acad. Sci. U. S. A* **2008**, *105*, 15654-15659.

[2] D. C. de Geus, E. A. J. Thomassen, P. L. Hagedoorn, N. S. Pannu, E. van Duijn, J. P. Abrahams, *J. Mol. Biol.*, **2009**, *387*, 192-206.

[3] T. Giblin, J. Frankenberger, *Microbiol. Res.* **2001**, *156*, 331-315.

## Application of Liteanu's frequentometric approach to estimate the qualitative limit of identification for some alkaline cations

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At the dawn of analytical chemistry, covering the qualitative identification of chemical species, the sensitivity of a given analytical reaction was judged by the limit of identification. The limit of identification has a major importance when it comes to precipitation and color analytical reactions. It is defined as the smallest detectable amount (or concentration) of a given analyte that could be identified with a specific analytical reagent, therefore, obtaining a positive identification reaction.<sup>[1]</sup> Friedrich (Fritz) Feigl—the father of spot tests—was the scientist that coined the concept of *limit of identification*, together with other characteristics such as selectivity, specificity and dilution limit. Nowadays, when analytical instruments are by far the most important approach in chemical analysis, the limit of identification has evolved into *limit of detection* since analytical signals are instrumentally measured.<sup>[2]</sup> The analytical procedure that could be applied to estimate the limit of identification for an analytical reaction is the Liteanu's frequentometric method.<sup>[3]</sup> This chemometric approach is based on a statistical interpretation of the experimentally-obtained values and aims to establish the value of the identification limit at a 99.7% positive frequency, above the uncertain analytical domain.

In this work, Liteanu's approach was applied on experimental data obtained for identification of some alkaline cations, including Li<sup>+</sup> and Cs<sup>+</sup>, as described in Fig. 1, using potassium iron(III) periodate for Li<sup>+</sup> detection and silicotungstic acid for Cs<sup>+</sup> detection. The values of the identification limits were compared with the detectability performances of alkaline cations using flame tests.

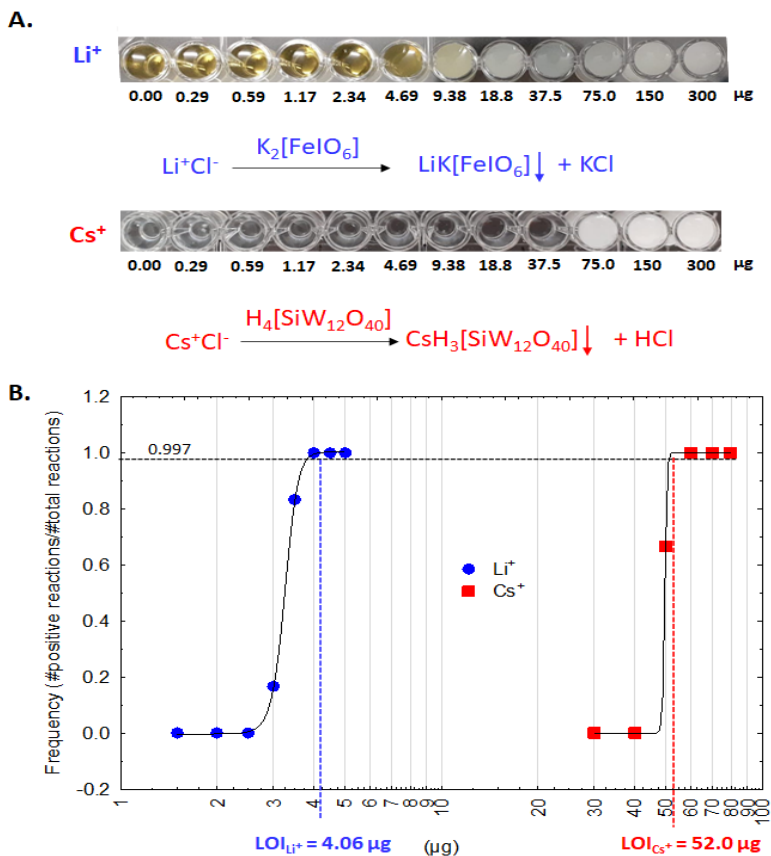


Fig. 1: Liteanu's frequentometric estimation of the *limit of identification* (LOI) in qualitative analytical chemistry of lithium and cesium. **A.** First experimental step involves an examination of the identification reaction over a wider concentration range. **B.** The second experimental step comprises of monitoring the frequency of the positive identification reactions over a shorter concentration domain, close to the LOI, in twelve replicates at each tested concentration, and statistical calculation of the LOI values using a sigmoidal fitting function.

- [1] M.T. Doménech-Carbó, A. Doménech-Carbó, *ChemTexts*, **2022**, 8, 1.  
 [2] M. Belter, A. Sajnog, D. Baratkiewicz, *Talanta*, **2014**, 129, 606.  
 [3] C. Liteanu, I. Rica, *Mikrochim Acta*, **1975**, 2, 311.

# The IDEAL (Immobilized DEhydrogenase for ALfa-keto-acids) tool for the synthesis of D-amino-acid

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Aromatic D-amino acids (D-AAs) have gained increasing attention in both industrial and pharmaceutical fields. Recently, biocatalytic procedures for the synthesis of D-AAs emerged as powerful and environmentally friendly methods. The utilization of D-amino acid dehydrogenase (D-AADH) for the biotechnological production of D-AAs has been limited due to the exclusive presence of useful L-AADH in natural resources. By the aid of protein engineering methods, recombinant D-AADH enzymes can be obtained using as template the *meso*-diaminopimelate dehydrogenase – D-APDH.<sup>[1]</sup>

The DAADH catalyzed enzymatic reaction, which provides D-AAs, requires the reduced form of nicotinamide adenine dinucleotide phosphate (NADPH) as a cofactor. In order to develop a cost-effective D-AADH-based synthetic procedure, cofactor regeneration is required, which can be achieved by using a parallel enzymatic system containing glucose dehydrogenase (GDH), which reduces  $\text{NADP}^+$  while oxidizing glucose.<sup>[1,2]</sup>

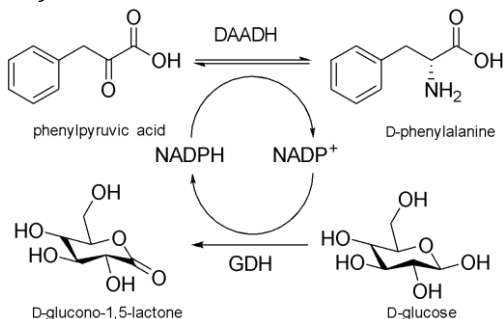


Fig. 1: The reductive amination of phenylpyruvic acid catalyzed by D-AADH coupled with the GDH mediated reaction.

Enzyme immobilization enables the recovery of the biocatalyst after the completion of the reaction and its recycling in a new catalytic cycle. On the other hand, immobilization often makes the biocatalyst usable in organic solvents and increases the enzyme's thermo- and pH stability.

In our work we optimized the immobilization method of D-AADH derived from *Ureibacillus thermosphaericus* (UtD-AADH), by testing several supports, different types of immobilizations, such as ionic interaction based fixation, covalent non-specific<sup>[3]</sup> and site-specific linkage<sup>[4]</sup>. Regarding the site-specific immobilization, several surficial serine residues positioned far from the active site were selected and successfully mutated to cysteines, thus ensuring the maleimide-thiol linkage.

Since the highest catalytic efficiency was obtained using the Purolite ECR8415F resin, we attempted to immobilize the D-AADH enzyme site-specifically onto the correspondingly functionalized Purolite resin (Fig. 2).

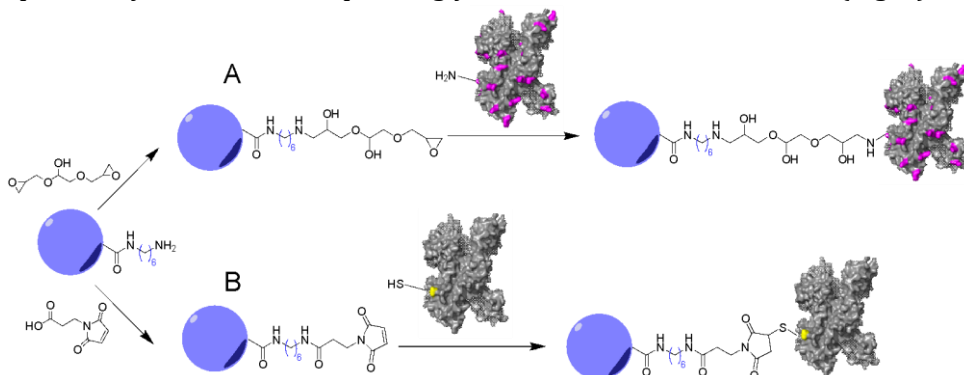


Fig. 2: Covalent immobilization of UtD-AADH onto Purolite ECR8415F resin via A) non-specific fixation of the enzyme through its surficial -NH<sub>2</sub> groups (from the lysine residues - pink) using glyceryl diglycidyl ether as linker and B) site-specific immobilization through single surficial cysteine residues (yellow) employing a maleimide-thiol linkage procedure.

- [1] H. Akita, J. Hayashi, H. Sakuraba, T. Ohshima, *Front. Microbiol.* **2018**, 9,1760.  
 [2] J. C. Moore, C. K. Savile, S. Pannuri, B. Kosjek, & J. M. Janey. *Comprehensive Chirality*, Elsevier Science, Amsterdam, **2012**.  
 [3] J. H. Bartha-Vári, L. C. Bencze, E. Bell, L. Poppe, G. Katona, F.-D. Irimie, C. Paizs, M. I. Toşa, *Period. Polytech. Chem. Eng.* **2017**, 61, 59.  
 [4] K. Boros, M. E. Moisă, C. L. Nagy, C. Paizs, M. I. Toşa, L. C. Bencze, *Catal. Sci. Technol.* **2021**, 11, 5553.

## DFT explorations of asymmetric (in)organic ethers/amines

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Inorganic ethers and amines, *i.e.* species displaying the  $(R_3E)_2O$  and  $(R_3E)_3N$  formulae ( $E = C, Si, Ge, Sn$ ), exhibit significantly different structural features compared to their organic counterparts.<sup>[1,2]</sup> These discrepancies were previously explained in terms of a bonding mechanism, which is based on offsets between the attractive secondary effects, *i.e.* vicinal  $LP(X) \rightarrow \sigma^*(E-R)$  hyperconjugations and  $LP(X) \rightarrow d(E)$  back-donations, and repulsive vicinal  $(LP(X) \cdots \sigma(E-E))$  Pauli interactions ( $X = O$  or  $N$ ;  $R = H, C$ , halogen, etc.).<sup>[3,4,5]</sup>

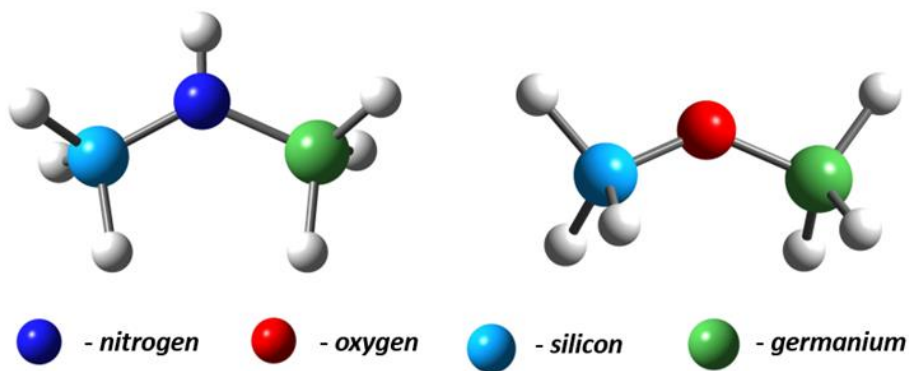


Fig. 1: Optimized structures of  $H_3Si-NH-GeH_3$  (left) and  $H_3Si-O-GeH_3$  (right) model derivatives.

The current research attempts to reinforce the previously developed theoretical model and aims at shedding light on asymmetric ethers and amines of the  $R_3E-O-E'R_3$  and  $R_3E-NH-E'R_3$  type ( $E, E' = C, Si, Ge, Sn$ ;  $E \neq E'$ ). In this regard, the molecular structures of several model systems (such

as the ones illustrated in Fig. 1) were optimized at the DFT level of theory, revealing patterns for the E–O–E' and E–N–E' moieties.

Additionally, natural bond orbital (NBO) analyses highlighted a tight correlation between the geometries of targeted species and the attractive-repulsive offset.

- [1] F. Weinhold, R. West, *Organometallics* **2011**, *30*, 5815.
- [2] F. Weinhold, R. West, *J. Am. Chem. Soc.* **2013**, *135*, 5762.
- [3] I.-T. Moraru, F. Teleanu, L. Silaghi-Dumitrescu, G. Nemeş, *Phys. Chem. Chem. Phys.* **2022**, *24*, 13217.
- [4] I.-T. Moraru, F. Teleanu, G. Nemeş, *J. Phys. Chem. A* **2020**, *124*, 8246–8253.
- [5] I.-T. Moraru, P. M Petrar, G. Nemeş, *J. Phys. Chem. A* **2017**, *121*, 2515–2522.



## Preparation and Characterization of thermal reduced 3D graphene oxide membranes

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Advanced material technology such as flexible electronic devices (e.g. sensors, supercaps, membrane sieves, solar panels, etc.) are in high demand for new materials with interesting morpho-structural and technical characteristics. A distinguished type of these are carbon nanomaterials that were identified as having a high potential to be involved in construction of devices with high level of technical performance, low cost and with capacity of miniaturization.

From the carbon nanomaterials, in the last two decades, graphene materials (e.g. graphene, graphene oxide, reduced graphene oxide, functionalized graphene oxide) were recognized as the most promising carbon nanomaterial class for technological development.<sup>[1]</sup> Among these, due to its possibility to be used as stable aqueous 2D nanosheet suspension, graphene oxide (oxidized form of graphene) is commonly involved in electronical applications

In this study, graphene oxide (GO) synthesized by an original sonochemical oxidation reaction followed by washing-centrifugation-decantation steps<sup>[2]</sup> is used as precursor aqueous suspension to obtain monolith 3D free-standing GO membranes. Afterwards, these electrical insulator materials were thermally reduced (100, 200 and 300°C) by an innovative method performed in ambient condition<sup>[3]</sup> to obtain reduced graphene oxide (rGO), (Figure 1). In this way, for rGO membrane thermally treated at 300°C for 10 min a decrease of the electrical resistivity around 740Ω/cm was obtained.

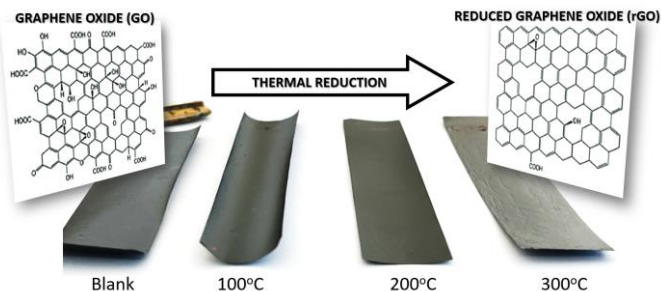


Fig. 1: Real image with graphene oxide (GO) and reduced graphene oxide (rGO) membranes.

The obtained monolith GO and rGO membranes were characterized by optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The obtained data confirm us the possibility to tune the electro-morpho-structural properties of the obtained membranes by changing the thermo-reduction conditions.

*Acknowledgements:* This work was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS/CCCDI-UEFISCDI, project number PN-III-P2-2.1-PED-2021-3156, within PNCDI III.

[1]

<https://www.graphene-info.com/europe-launches-1-billion-graphene-flagship-project>

[2] L.C. Cotet, K. Magyari, M. Todea, M.C. Dudescu, L. Baia, V. Danciu, Versatile self-assembled graphene oxide membranes obtained under ambient conditions by using a water-ethanol suspension J Mater Chem A 5, 2132 2017

[3] L.C. Cotet, V. Danciu, L.G. Baia, Process for preparing graphene-based materials on very large surfaces by chemical exfoliation, Patent OSIM, RO131216A2 (B1)/2016-06-30.

## Protein engineered phenylalanine ammonia-lyase from *Arabidopsis thaliana*: setting the ground for site-specific immobilization

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The creation of synthetic processes based on biotransformations has advanced dramatically in recent years, enabling technologies with increased efficacy, productivity and selectivity, reduced costs and environmental footprint. In addition to high catalytic activity and selectivity, key requirements for successful application of enzymes in synthetic processes are stability and recyclability, generally achieved through enzyme immobilization. Due to the recent impressive advances in protein engineering and protein structural analysis, efficient site-specific enzyme immobilization techniques have arisen<sup>[1]</sup>, overcoming the limitations of non-specific covalent immobilization, such as inability to control the number of formed covalent bonds and the orientation of the enzyme attached to the support, providing increased biocatalytic activity. A simple, versatile and efficient approach for site-specific enzyme immobilization, consists in the maleimide/thiol coupling of engineered enzymes with cysteine residues introduced at selected positions on the enzyme surface, to maleimide-functionalized supports, affording highly stable and active biocatalysts.

Phenylalanine ammonia-lyases (PALs), naturally catalyzing the non-oxidative deamination of L-phenylalanine to *trans*-cinnamic acid, are already well-established biocatalysts for the production of both D- and L-phenylalanine derivatives<sup>[2]</sup>, useful building blocks in medicinal and synthetic chemistry. PAL from *Arabidopsis thaliana* (AtPAL) recently proved to be superior to the well-studied PAL from *Petroselinum crispum* in the biotransformation of several substituted phenylalanine and *trans*-cinnamic acid analogues.<sup>[3]</sup>

In this context, motivated by the previous successful site-specific immobilization of PcPAL<sup>[4]</sup>, we focused our research on developing the site-

specific immobilization of AtPAL through maleimide/thiol coupling, with the aim of developing efficient processes for the synthesis of optically pure phenylalanines.

Accordingly, the sequence alignment of AtPAL and PcPAL was first performed, revealing high sequence identity (81%) and identical catalytic sites, as well as additional Cys residues supposedly located at the surface of AtPAL. Since the successful application of the maleimide/thiol immobilization method is conditioned by the lack of cysteine residues at the surface of the enzyme, five surficial Cys residues were mutated to Ser, the isolated mutant enzyme demonstrating comparable enzymatic activity to the wild-type variant, supporting that the mutations did not affect the overall protein folding. Moreover, by analogy to PcPAL, two sites for immobilization, S615 and S391, were selected and replaced by Cys, obtaining two site-specifically immobilized biocatalysts, which were compared in terms of catalytic activity and recyclability to the non-specific covalently immobilized AtPAL.

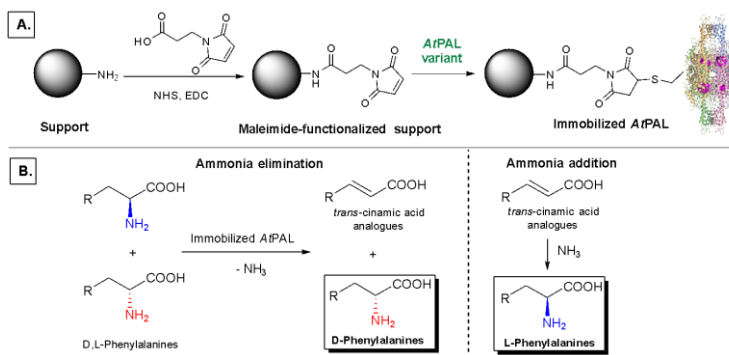


Fig. 1: Site-specific immobilization of AtPAL (A) and bioprocesses for the synthesis of optically pure phenylalanines (B)

### Acknowledgements:

This work was financed by the National Research Council-UEFISCDI, project number: PN-III-P1-1.1-PD-2019-1188, PD 68/2020.

- [1] F. A. Al-Lolage, P. N. Bartlett, S. Gounel, P. Staigre, N. Mano, *ACS Catal.* **2019**, 9, 2068.
- [2] F. Parmeggiani, N. J. Weise, S. T. Ahmed, N. J. Turner, *Chem. Rev.* **2018**, 118, 73.
- [3] S. D. Tork, M. E. Moisă, L. Cserepes, A. Filip, L. C. Nagy, F. D. Irimie, L. C. Bencze, *Sci. Rep.* **2022**, 12(10606), 1.
- [4] K. Boros, M. E. Moisă, C. L. Nagy, C. Paizs, M. I. Toşa, L. C. Bencze, *Catal. Sci. Technol.* **2021**, 11, 5553.

# Towards the Active-Template Synthesis of *N*-Heterocyclic Carbene-Based [2]Rotaxanes

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Rotaxanes represent a type of mechanically interlocked molecules (MIMs) that have important applications as molecular devices for information storage and processing, and were extensively exploited for the construction of functional artificial nanomachines.<sup>[1]</sup> Moreover, this type of challenging molecules have been used in supramolecular and homogeneous catalysis.<sup>[2]</sup>

Basically, a [2]rotaxane is comprised of an axle, two stoppers, and a macrocycle whose movement along axle is controllable.<sup>[1]</sup> There are several ways to construct rotaxanes, such as active metal template synthesis, the metal playing a double role during the construction of the interlocked molecule: as template for interlacing the components and as catalyst for detaining the final component by bond formation.<sup>[3]</sup> On the other hand, *N*-heterocyclic carbenes (NHCs) are generally used in chemical transformations, acting both as organocatalysts or, as ligand for transition metals, catalyst in a diversity of coupling reactions.<sup>[4,5]</sup>

In this context, we consider of interest to design a [2]rotaxane embedding a NHC moiety in the axle part (Fig. 1), in order to boost the catalytic activity of the Cu(I) metallic center. In this line, our proposed strategy for obtaining the desired [2]rotaxane involved the synthesis of two key intermediates: a macrocycle precursor and a dumbbell (axle + stoppers) segment. Herein, we present the synthesis of the last key intermediate (*i.e.* dumbbell) by a click reaction between the stoppers and a functionalized *N*-heterocyclic carbene derivative. This reaction is based on copper(I)-catalysed terminal alkyne–azide cycloaddition (the CuAAC “click” reaction), which demonstrated to be a powerful tool for the construction of mechanically interlocked architectures.<sup>[6]</sup> The reaction was completed under mild conditions, and resulted in 1,2,3-triazoles.

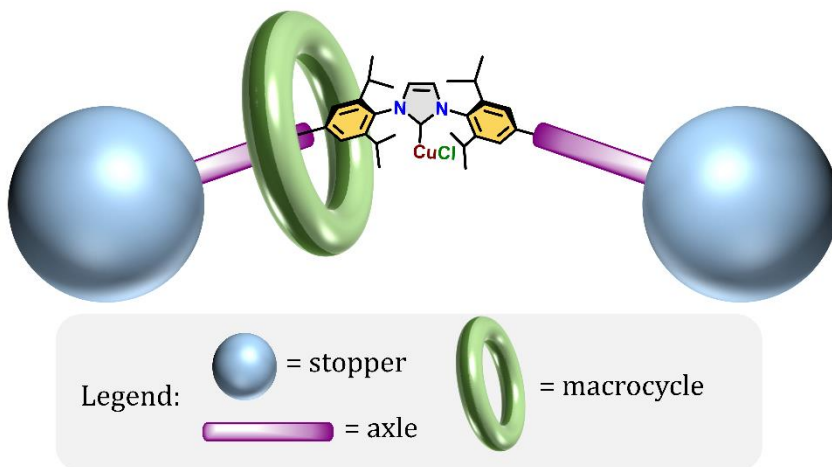


Fig. 1: Schematic representation of the target [2]rotaxane

The intermediate compounds have been characterized by NMR spectroscopy and the dumbbell target was analyzed by high-resolution mass-spectrometry.

With the dumbbell molecule in hand, we are now focused on the synthesis of the macrocycle part, to interlock it with the dumbbell building block to obtain the proposed NHC-based [2]rotaxanes.

- [1] M. Xue, Y. Yang, X. Chi, X. Yan, F. Huang, *Chem. Rev.* **2015**, *115*, 7398–7501.
- [2] D. A. Leigh, V. Marcos, M. R. Wilson, *ACS Catal.* **2014**, *4*, 4490–4497.
- [3] J. D. Crowley, S. M. Goldup, A.-L. Lee, D. A. Leigh, R. T. McBurney, *Chem. Soc. Rev.* **2009**, *38*, 1530–1541.
- [4] Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.* **2020**, *120*, 1981–2048.
- [5] J. D. Egbert, C. S. J. Cazin, S. P. Nolan, *Catal. Sci. Technol.* **2013**, *3*, 912.
- [6] K. D. Hänni, D. A. Leigh, *Chem. Soc. Rev.* **2010**, *39*, 1240–1251.

# Synthesis and photophysical analysis of phenothiazine-based symmetric and non-symmetric curcuminoids and their boron complexes

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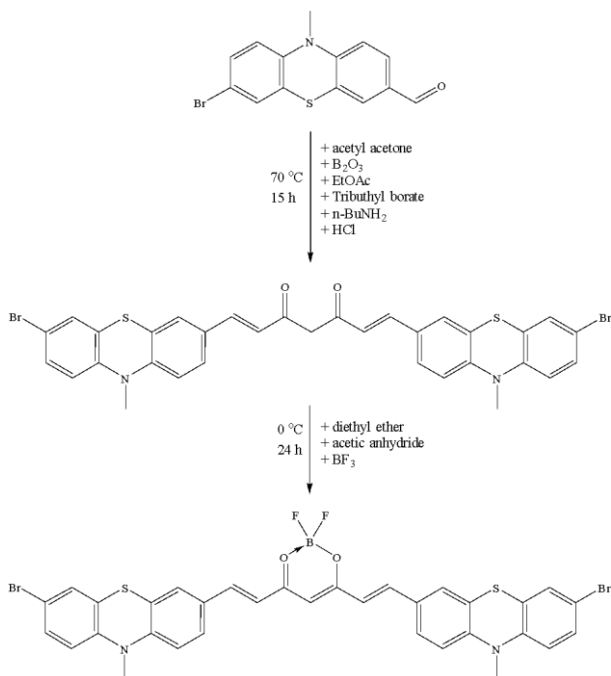
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Before the advent and development of medicine, mankind tried to fight diseases with extracts from certain plants, one of the most commonly used being turmeric. The medicinal active substance extracted from turmeric is called curcuminoid, which has a chemical structure consisting of a double-sided linkage of aromatic aldehyde derivatives to acetylacetone.

Curcumin derivatives exhibit good optical and electrical properties owing to a highly  $\pi$ -electron delocalized system, by changing the aromatic groups at the end of the diketone the photophysical properties can be tuned.<sup>[1]</sup>

It is well known that phenothiazine exhibits a rigid structure with a large conjugated system and it has strong electron donor properties due to the presence of electron-rich nitrogen and sulfur in the central ring. In addition, the ability to functionalize the phenothiazine at multiple positions allows the fine-tuning of the photophysical properties of the molecule. Therefore phenothiazine-based curcuminoid derivatives have the potential to be excellent candidates for designing materials used in organic electronic applications, for example as a dye for DSSC third-generation solar cells. The  $\beta$ -diketone group possesses a crucial characteristic: the capacity to generate chelates with various metals and metalloids, such as boron<sup>[2]</sup>. By integrating  $\text{BF}_2$  into the curcumin molecules, the durability of the 1,3-diketone unit is amplified, leading to improved stability and a bathochromic shift in both absorption and emission spectra. These advantages have necessitated the preparation of boron complexes of curcumin derivatives for organic electronic applications.



**Scheme. 1:** Synthesis of phenothiazine-based symmetric curcumin and its boron complex

Synthesis of phenothiazine-based symmetric (Scheme 1) and non-symmetric curcumins and their complexation with boron, followed by their photophysical and structural analysis by FT-IR, HRMS, NMR, and UV-Vis methods were accomplished.

## References

- [1] S. Prasad, D. DuBourdieu, A. Srivastava, P. Kumar, R. Lall, *Int. J. Mol. Sci.*, **2021**, 22, 7094.
- [2] P. Peni, R. Sasri, I. H. Silalahi, *J. Kim. Sains Apl. (J. Sci. Appl. Chem.)*, **2020**, 23(3), 75.



# Synthesis of the alkyl fluorene derivatives and study of their photophysical properties

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At the mid-20<sup>th</sup> centuries, the importance of the solar technologies has been growing at a high rate, thanks for the success of the space explorations. At the 50-s the electric power was stored in chemical batteries, which has a big volume and weight. To solve this type of engineering problem, scientists have invented solar cells. The operating principles of solar cells depend on the photovoltaic effect: a semiconductor is radiated by light, absorbs energy, and generates an electric current.<sup>[1,2]</sup>

The semiconductors absorption properties are not the best if we consider the power usage. These properties can be changed by a dye layer on the surface of semiconductors. The dyes can be separated to a chromophore and an auxochrome base. The chromophore base is responsible for the light absorption intensity, the auxochrome base corresponds for the absorption range.

During my research work, first, we synthesize bromo- and carbonyl-alkyl fluorenes as a starting material for a condensed alkyl fluorene-based dye. These types of compounds can be used as biomarkers, but in most research work are described as raw material for Organic Light Emitting Diode (OLED) or starting material for DSSC compounds.<sup>[3]</sup>

My research is focused on synthesizing alkyl fluorene-based dye molecules, the reaction route is presented on Figure 1. The resulting product can be used as a dye material for dye-sensitized solar cells (DSSC).

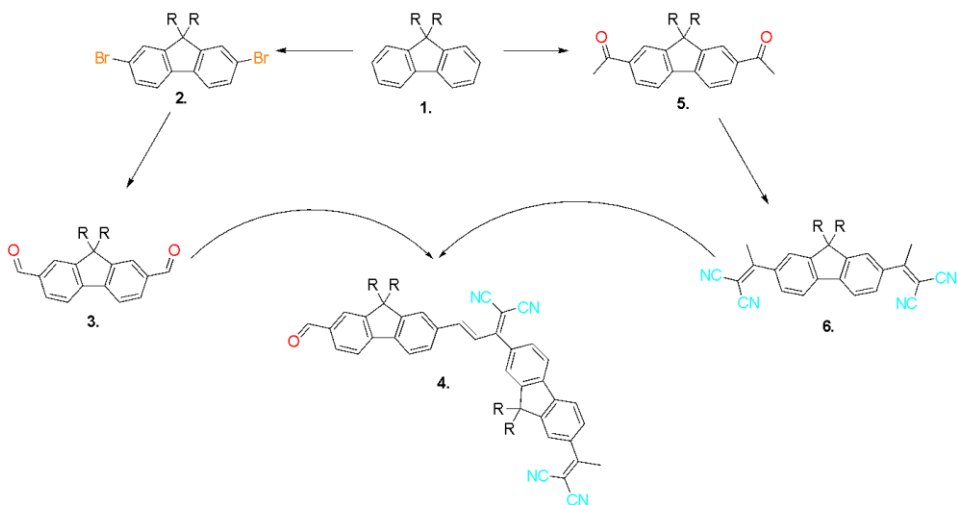


Figure 1. Synthesis route of the alkyl fluorene into a dye compound

[1] M. M. Koltun, *Sol. Energy Mater. Sol Cells* **1996**, *44*, 293–317.

[2] J. Luther, M. Nast, M. N. Fisch, D. Christoffers, F. Pfisterer, D. Meissner, J. Nitsch, *Ullmann's Encyc. of Ind. Chem.* **2016**, *7*, 17667–17718.

[3] K. R. J. Thomas, A. Baheti, *Mater. Technol.* **2013**, *28*, 71–87.

# Chemical interface damping of surface plasmon resonance in silver nanoparticles: effects of amino acid and thiol molecules adsorption

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The decay of excited plasmons in metallic nanoparticles can be caused by radiative or nonradiative mechanisms.<sup>[1]</sup> Chemical interface damping (CID) is a process that involves coherent electron oscillations and occurs when electrons scatter at the surface of the nanoparticle and transfer energy to adsorbate energy levels.<sup>[2]</sup> Using dark field microscopy, we analyze the CID of surface plasmon resonance (SPR) modes in single AgNPs and monitored changes in the SPR band's position and half width at half maximum (hwhm) after adding amino acids and thiol molecules (Fig. 1).

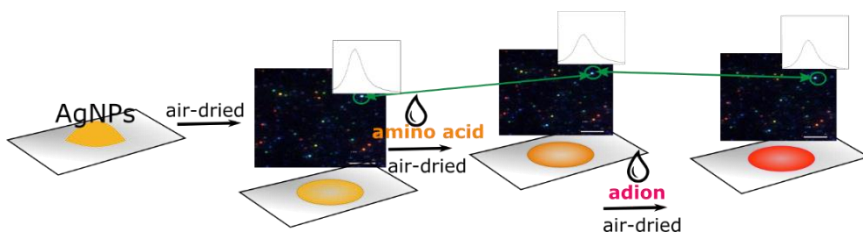


Fig. 1: Schematic representation of the experimental methodology.

When leucine is added to AgNPs, the SPR band significantly shifts ( $p=0.05$ ) from 538.2-530.1 nm. Moreover,  $\text{Ca}^{2+}$  enhance the adsorption of leucine onto AgNPs causing an additional significant red shift (530.1-551.8 nm) and a broadening of the SPR band ( $p=0.05$ ), indicating a CID effect. Similarly, the addition of phenylalanine to AgNPs causes a shift in the SPR band ( $p=0.002$ ) but no hwhm variation. When  $\text{Ca}^{2+}$  is added, there is a further shift in the SPR band (577 nm) and a widening of the band.

In contrast, thiol molecules (cystine, thiobenzoic acid, 4-mercaptobenzoic acid) that spontaneously adsorb onto AgNPs lead to a significant red shift (more than 40 nm) and broadening of the SPR band of AgNPs (approximately 20 nm). The sequential addition of  $\text{Ca}^{2+}$  does not influence the CID effect in the thiol-AgNPs complex.

Our results show that the spontaneous adsorption of thiol molecules to AgNPs leads to a CID effect, whereas in case of leucine and phenylalanine adions are required for the adsorption of these amino acids to AgNPs and give rise to CID.

- [1] C. Sönnichsen, *Plasmons in Metal Nanostructures*, Cuvillier Verlag, **1998**.
- [2] S. W. Moon, J. W. Ha, *Physical Chemistry Chemical Physics* **2019**, 21, 7061.

# Assessment of Raman enhancement of water soluble carotenoids by metal nanoparticles

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Carotenoid levels have been identified as SERS liquid biopsy markers in various diseases, but their characteristic bands have been interpreted as either resulting from Resonance Raman (RR) or SERS effects. Some studies suggest that hydrophilic carotenoids have a greater affinity for metal nanoparticles.<sup>[1]</sup> Our study aimed to systematically assess the nature of the water-soluble carotenoid signal in the presence of metallic nanoparticles (NPs).

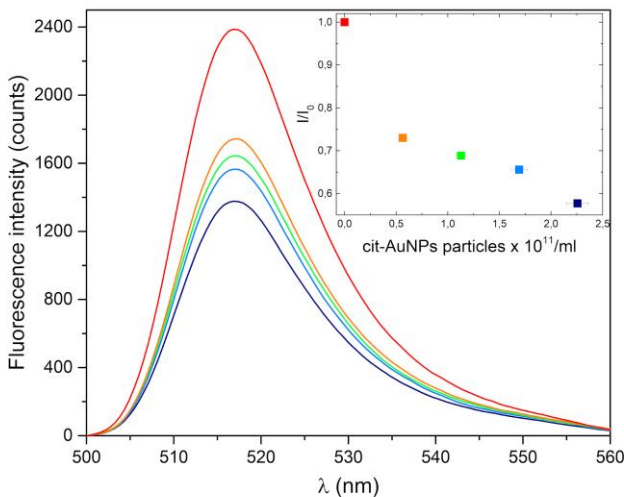


Fig. 1: Fluorescence emission of free, unbound beta-carotene at different AuNPs concentrations, indicating a higher adsorption of beta-carotene to the Au surface, with increasing AuNP concentration.

We used norbixin and a water-soluble analogue of nature-identical beta-carotene (E 160a(i)) and acquired Raman spectra of the carotenoid solutions using silver nanoparticles (AgNPs), in the resonance domain of the carotenoids and gold nanoparticles (AuNPs) out of resonance. We also monitored the adsorption of beta-carotene using fluorescence spectroscopy. Solutions of colloidal AuNPs with different NP concentrations ( $0 - 2,26 \times 10^{11}$  particles/ml) were prepared for identical beta-carotene concentrations, and the fluorescence signal from carotenoid in the supernatant was measured after removing nanoparticles through centrifugation.

The characteristic Raman bands were first detected in solution through Resonance Raman. The presence of metallic nanostructures enhanced the spectra of water-soluble analogue of beta-carotene, in both the resonance and out of resonance excitation regimes. Using AgNPs with an excitation wavelength at 532 nm that fits both the resonance condition of beta-carotene and the surface plasmon resonance (SPR) of AgNPs enhanced the Raman bands of beta-carotene. Exciting only the SPR of AuNPs using a 633 nm laser line resulted in a lower enhancement of beta-carotene bands.

Under resonance conditions for the norbixin solution in the presence of AgNPs, SERS enhancement was observed. However, exciting only the SPR of AuNPs did not result in any enhancement of norbixin signal.

Fluorescence measurements on beta-carotene showed a decrease in the fluorescence signal of carotenoid in the supernatant with the increase of the colloid concentration (Fig. 1). This trend suggests the gradual increase in adsorbed carotenoid molecules.

Concluding, the enhancement of norbixin and water-soluble beta-carotene bands resulted from the SERS effect in the presence of metallic nanoparticles. In addition, fluorescence measurements suggested carotenoid adsorption to metal nanoparticles.

# Analysis of the pH dependence of Ferryl Myoglobin reactivity using UV-Visible spectrometry

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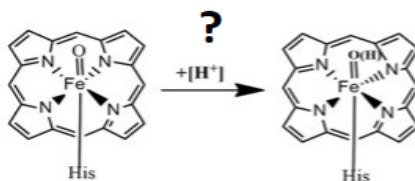


Fig. 1: Ferryl Mb protonation

The ferryl species consist of an oxo ligand bound to iron,  $\text{Fe}^{\text{IV}}=\text{O}$ . In heme systems, especially in heme-containing proteins, this is known as Compound II and is part of a large range of biologically important processes (e.g. the catalytic cycle of the abundant liver enzymes, cytochromes P450, or the mechanisms of defence against oxidative stress in peroxidases and catalases, or a series of important side-reactions of hemoglobin and myoglobin).<sup>[1]</sup>

Several experiments have set out to discover if the ferryl heme in proteins is better formulated as an (unprotonated)  $\text{Fe}^{\text{IV}}=\text{O}$  or as a (protonated)  $\text{Fe}^{\text{IV}}-\text{OH}$  (Fig. 1), see [1] and [2] for example. One area where this aspect is extremely important relates to the fact that *in vivo* the ferryl Mb and Hb are highly reactive, especially in strongly acidic environments.<sup>[3]</sup>

In this study, following the procedure in [5], we have analysed the Soret, alpha and beta bands of ferryl Mb in terms of pH. We have used UV-Visible spectrophotometry to monitor the stability of ferryl Mb in time and to observe the formation of ferryl Mb in terms of the quantity of hydrogen peroxide used in the reaction with met Mb. For pH-jump experiments, we have used the stopped-flow technique. A solution of met Mb was mixed with a 10-fold excess of  $\text{H}_2\text{O}_2$ . The ferryl Mb species that was formed was analysed for ~2 seconds while it was mixed with buffer solutions whose pH values ranged from 2 to 10. Concomitantly, the stability of the ferryl Mb solution was monitored throughout the stopped-flow experiment using the

UV-Visible spectrophotometer and it was observed that it remained constant at all times.

The results show that in the pH range 6-10 the spectrum of the ferryl Mb does not change. The spectrum of the Soret band in this case has a maximum absorption at 422.5 nm. In contrast, the spectrum recorded at pH 2

shows a significant shift of ~27 nm associated with protein denaturation. In addition, the spectra collected at pH 3, 4 and 5 have the exact same hypsochromic shift of ~3 nm compared to pH 6-10.

At 500-600 nm, the typical alpha and beta bands of the heme also experience a hypsochromic shift upon going from pH 5-10 to pH 3-4 – but now much larger than the one seen for the Soret band (ca. 20 nm for the alpha band and ca. 40 nm for the beta band).

The results show that ferryl Mb clearly depends on pH. At alkaline and neutral pH, ferryl Mb is stable (e.g. at pH 9-10 it is stable for at least 1-2 hours). At strongly acidic pH, the species is highly unstable, which is correlated with an increased reactivity that is most likely due to the protonation at or near the Fe=O unit. The fact that the ferryl oxygen is more likely to be protonated than the nitrogen atom from the distal histidine is supported by numerous studies, see [1] and [4] for instance. Nevertheless, the prevailing hypothesis in the literature is that the protonation phenomenon that we describe here with stopped-flow UV-Visible spectroscopy does not occur directly at the FeO unit, but rather at a hydrogen bonding partner of the FeO oxygen.<sup>[1]</sup> The very small hypsochromic shift that we describe here for the first time may be taken as to support this leading hypothesis – that the protonation of ferryl Mb at acidic pH does not occur directly at the oxygen. On the other hand, the large alpha and beta hypsochromic shifts support our alternative hypothesis – that ferryl Mb below pH 6 is protonated to Fe<sup>IV</sup>-OH.

[1] R. K. Behan, M. T. Behan, *On the status of ferryl protonation*, *J. Inorg. Biochem.*, **2006**, 100 (4), 448-459.

[2] P. C. E. Moody, E. L. Raven, *The Nature and Reactivity of Ferryl Heme in Compounds I and II*, *Acc. Chem. Res.*, **2018**, 51 (2), 427-435.

[3] B. J. Reeder, M. A. Sharpe, A. D. Kay, M. Kerr, K. Moore, M.T. Wilson, *Toxicity of myoglobin and haemoglobin: oxidative stress in patients with rhabdomyolysis and subarachnoid haemorrhage*, *Biochem. Soc. Trans.*, **2002**, 30 (4), 745-748.

[4] R. Silaghi-Dumitrescu, *The nature of the high valent complexes in the catalytic cycles of hemoproteins*, *J. Biol. Inorg. Chem.*, **2004**, 9 (4), 471-476.

[5] R. Silaghi-Dumitrescu, B. J. Reeder, P. Nicholls, C. E. Cooper, M. T. Wilson, *Ferryl haem protonation gates peroxidatic reactivity in globins*, *Biochem. J.*, **2007**, 403 (3), 391-395.



# Determination Of Electrophoretic Mobilities On Agarose

## For Some Dyes And Their Correlation With Theoretically Predicted Values

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Gel electrophoresis (GE) is a robust technique used to distinguish and separate solvated ionic, molecular, or colloidal charged chemical species based on their electrophoretic mobilities. In this method, the species are introduced into wells in a nanoporous and flexible gel, which is then immersed in an electrolyte buffer solution. An electric field is then applied between two inert electrodes. In the examination of polyanionic DNA and RNA, GE is an extremely vital technology that allows for high-resolution measurements of polynucleic acid lengths.

The present study aims to measure the electrophoretic mobilities of some dyes using GE in agarose. In addition, this analytical technique is valuable to calculate different stability constants by a novel approach.<sup>[1]</sup> By examining the electrophoretic mobilities of dyes, this study provides insights into the characteristics and behavior of these molecules. The experimentally determined electrophoretic mobilities of the studied dyes, comprising of varied sizes and charges were compared with predicted values, as indicated in Fig. 2, according to the equation below, as previously described.<sup>[2]</sup>

$$\mu_{e,pred} = \frac{q}{C\eta_{eff}a} \quad \mu_{e,meas} = \frac{v}{E}$$

$\mu_{e,pred}$ -predicted electrophoretic mobility, q-molecular

charge

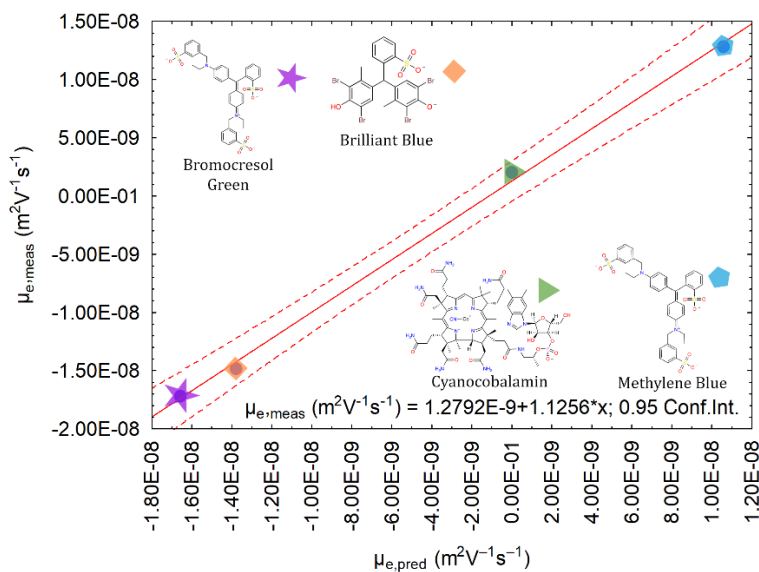
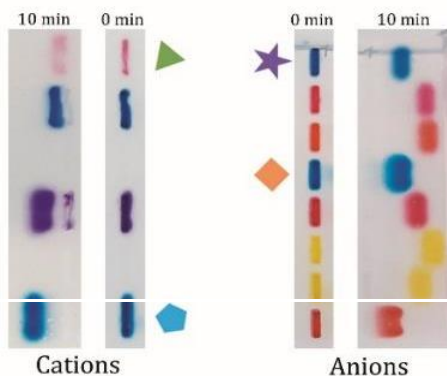
$C=4\pi$  for slip and  $C=6\pi$  for stick boundary conditions

$\eta_{eff}$ -the effective viscosity of the liquid outside the molecules in the porous gel

a-translational hydrodynamic radius of a given dye

$\mu_{e, meas}$ - measured electrophoretic mobility, v-average velocity of the molecule

E- electric field in the linear propagation regime



[1] Dimitri A. Bikos, Thomas G. Mason, *Nat. Commun.*, **2019**, *10*, 3631.

[2] Pernodet, N., Maaloum, M. & Tinland, B, *Electrophoresis*, **1997**, *18*, 55-58.

## The role of diphosphoalkenyl derivatives with P(III)=C-P(V) groups for stabilizing coordinative compounds.

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Prof. Dr. Gabriela Nicoleta NEMEȘ<sup>2</sup>*

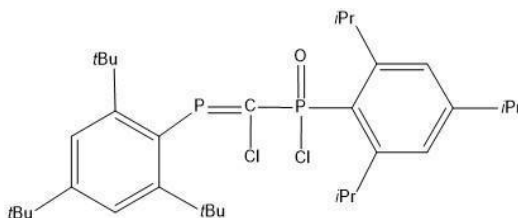
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The chemistry of unsaturated compounds containing 1,3-diphosphoalkenyl –P=C-P moiety maintains its scientific interest due to the applications of these compounds, especially in coordinative chemistry.<sup>[1]</sup> By oxidizing P=C-P derivatives, rich electron species P=C-P=Y (Y = O, S) can be obtained; such compounds are able to act as ligands with multiple coordination sites.

Following previous literature,<sup>[2]</sup> the P=C-P=O species (Scheme 1) was reacted with transition metal fragments such as PdCl<sub>2</sub>(CNMe)<sub>2</sub> in both dichloromethane and toluene as solvents.

In the case of PdCl<sub>2</sub>(CNMe)<sub>2</sub>, the reaction was almost quantitative after 2 hours. The product was characterized in solution by <sup>31</sup>P NMR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. The findings suggest that the obtained compound is not stable for more than 24 hours, even in an inert atmosphere.



Scheme 1

The reactivity of the newly obtained compounds and their complete characterization is under investigation.

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- [1] H. Liang, S. Ito, M. Yoshifuji, *Org. Lett.*, **2004**, 6, 452.
- [2] R. Şeptelean, G. Nemeş, J. Escudié, I. Silaghi-Dumitrescu, H. Ranaivonjatovo, P. Petrar, H. Gornitzka, L. Silaghi-Dumitrescu, N. Saffon, *Eur. J. Inorg. Chem.*, **2009**, 628.

## Oldies but Goldies: Exploring an Ancestral L-amino acid oxidase towards unnatural L-phenylalanine analogues

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L-amino acid oxidases (LAAOs) are enzymes that contain flavin adenine dinucleotide (FAD) cofactor and facilitate the stereospecific oxidation of L-amino acids (**1**), leading to the formation of imino intermediates (**2**), which through hydrolysis result in the production of the corresponding  $\alpha$ -keto acids (**3**) and ammonia. The reduced FADH<sub>2</sub> is reoxidized by molecular oxygen, resulting in the formation of hydrogen peroxide.

The biocatalytic applications of LAAOs have been limited by their restricted substrate tolerance, low recombinant expression levels, and the absence of appropriate activity screen methods.<sup>[1]</sup> However, the recently developed ancestral LAAO (AncLAAO)<sup>[2]</sup> addresses these limitations and becomes a promising candidate for amino acid deracemization, the development of chemo-enzymatic cascades, and hydrogen peroxide-based high-throughput activity screens.

This study aimed to assess the activity of AncLAAO towards a variety of phenylalanine analogues with different substituents. The activity was monitored based on the hydrogen peroxide degradation reaction catalyzed by horseradish peroxidase (HRP), quantifying spectrophotometrically the red quinoneimine dye resulted from the condensation of 4-aminoantipyrine and vanillic acid (Figure 1). The results revealed that AncLAAO efficiently catalyzes the oxidative deamination of mono-, di-, or multiple *meta*- or *para*-substituted phenylalanines, while *ortho*-substituted substrates were poorly transformed due to steric hindrance within the catalytic site. These findings provide important insights into the substrate domain of AncLAAO, which significantly overlaps with the substrate scope of phenylalanine ammonia-lyases (PALs). Furthermore, an efficient high-throughput solid-phase assay

used to identify variants of PAL with enhanced activity toward unnatural L-phenylalanines was developed by a coupled AncLAAO-PAL solid-phase enzyme assay. This offers a facile screening tool for further directed evolution studies of PALs<sup>[3]</sup>, highlighting the versatility of AncLAAO and its importance in such studies.

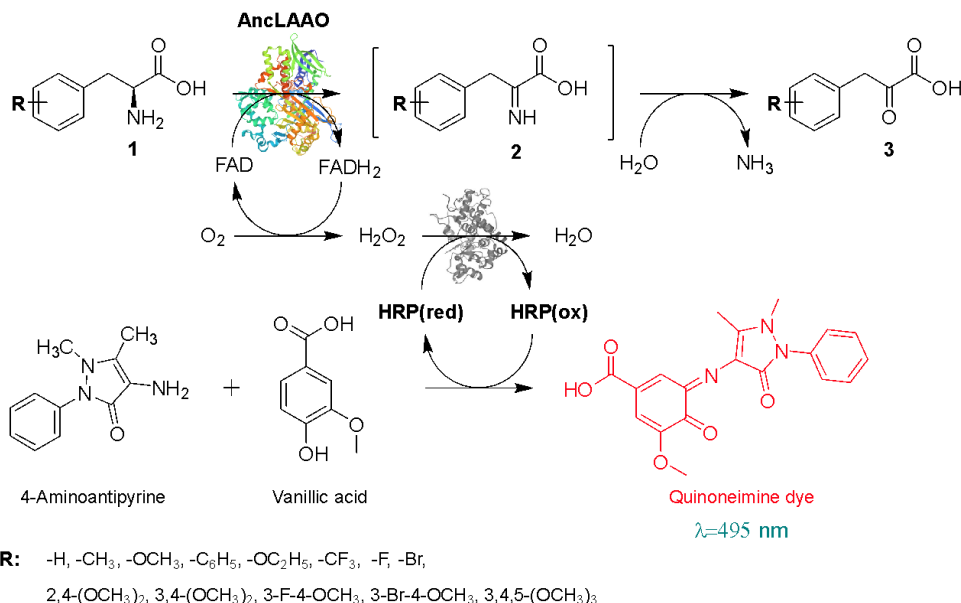


Fig. 1: General overview of the high-throughput assay employed in the catalyzed oxidative deamination of phenylalanine analogues performed by AncLAAO

[1] D. Bifulco, L. Pollegioni, D. Tessaro, S. Servi, G. Molla, *Appl. Microbiol. Biotechnol.* **2013**, 97, 7285.

[2] S. Nakano, Y. Minamino, F. Hasebe, S. Ito, *ACS Catal.* **2019**, 9, 10152.

[3] F. Parmeggiani, S. L. Lovelock, N. J. Weise, S. T. Ahmed, N. J. Turner, *Angew. Chem., Int. Ed.* **2015**, 54, 4608.

# **Mathematical Modeling of the Production Process of Polyvinyl Alcohol, Polylactic Acid and Polycaprolactone Nanofibers by Electrospinning Process**

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Polymers are macromolecules with versatile structures, compositions, and properties, which make them useful in a wide range of applications, including biophysics, medicine, and electronics. Biocompatible polymers, in particular, are notable for their easy processability and sterilizability, longer shelf life and light weight. In our work we studied biocompatible polymers: polyvinyl alcohol (PVA), polylactic acid (PLA) and polycaprolactone (PCL).

Our goal was to use factorial design experiments to predict the diameter of nanofibers made from PCL, PLA and PVA, while adjusting various parameters. Factorial design experiments are a powerful tool that allows for the exploration of multiple factors and their interactions in a systematic and efficient way. By carefully selecting and manipulating various manufacturing factors, we can create a range of experimental conditions that will help identify the most important parameters that contribute to nanofiber diameter. By conducting these experiments and analyzing the results using statistical methods, we can gain a deeper understanding of the relationship between the parameters and nanofiber diameter and use this information to optimize the production of nanofibers for a variety of applications.

Electrospinning is a fast, efficient, and inexpensive method for producing micro- and nanometer-range polymer fibers. Depending on the type of polymer, the resulting structure can have improved physical properties such as smaller pore size, larger porosity, larger surface-to-volume ratio, three-dimensional features. Structural properties also depend on experimental conditions such as concentration, applied voltage, needle-collector distance, flow rate. Different polymers require unique process parameters. Electrospinning can produce a variety of fibers with different diameters and morphologies, which can be used in various

applications such as tissue engineering, drug delivery, wound healing, and biosensors.<sup>[1]</sup>

Experimental design is the process of conducting research in an objective and controlled manner to maximize accuracy and draw concrete conclusions regarding a hypothesis. Typically, the goal is to determine the effect of an independent variable or factor on a dependent variable. It is particularly useful because it requires relatively few experiments per parameter studied; the interpretation of observations generated by the designs can largely be done using common sense, elementary arithmetic, and computer graphics. When the factors are quantitative but are not capable of fully exploring a large region of the factor space, promising directions for further experimentation can still be determined. Additionally, the designs are easily expandable when examination of another area is needed. In this project, we use experimental design to optimize the diameter of threads with minimal experiments.<sup>[2]</sup>

Based on the experiments performed, it can be said that concentration and flow rate have the greatest effect on the fiber diameter, and distance and voltage the least. It is important to note that the optimal combination of parameters for each polymer type was different, highlighting the need for a systematic approach in the optimization process. The results obtained through the factorial design experiment can be used to predict the fiber diameter of each polymer type under different experimental conditions, allowing for more efficient and effective production of nanofibers with specific properties. Further research can be conducted to explore the effects of other parameters on the fiber diameter, such as temperature and humidity, to obtain a more comprehensive understanding of the electrospinning process and optimize the production of nanofibers.

Overall, biocompatible polymers and electrospinning are promising technologies for developing new materials that can be used in various medical applications. The versatility of these materials and techniques allows to produce customized materials with specific properties and structures, which can improve their effectiveness and efficiency in medical applications.

[1] S. Agarwal, J. H. Wendorff, A. Greiner, Use of electrospinning technique for biomedical applications, *Polymer*, **2008**, 49, 26, 5603-5621

[2] G. E. P. Boks, J. S. Hunter, W. G. Hunter, Statistics for Experimenters Design, Innovation, and Discovery, 2nd edition, Hoboken, *John Wiley & Sons, Inc.*, **2005**



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